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Part 2

Fifth Edition

Edited by
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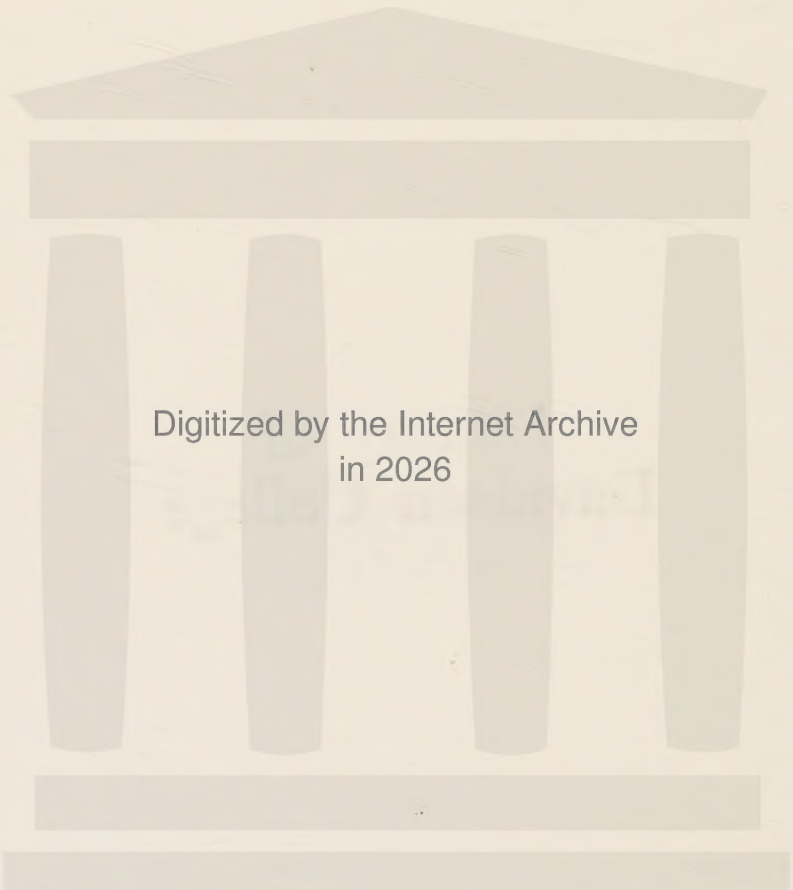
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MODERN PETROLEUM TECHNOLOGY

THE INSTITUTE OF PETROLEUM

The Institute acquired its crest,
designed by the College of Heralds, in 1949
Its motto, 'Conjunctione Potiores'
(strength through unity),
supports a shield portraying
the Archaeopteryx, an avian fossil
which was found in Jurassic strata
similar in age to important oil-bearing formations
in the North Sea

MODERN PETROLEUM TECHNOLOGY

5th Edition
Part II

Edited by

G. D. Hobson
B.Sc., Ph.D., D.I.C., F.G.S., A.R.S.M., S.P.E.,
A.A.P.G., F.Inst.Pet.

on behalf of
The Institute of Petroleum, London

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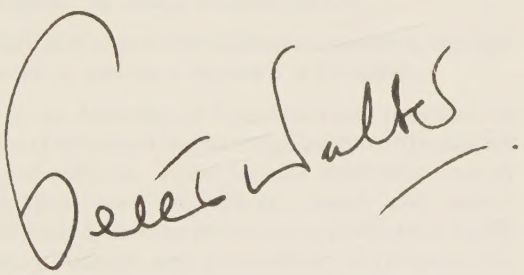
FOREWORD

I am pleased to have been asked to write a foreword to this new edition of 'Modern Petroleum Technology'. It is eleven years since the previous edition of this authoritative oil handbook, produced by the Institute of Petroleum, was first published. In that period, fundamental changes have occurred in the energy field and to the vital role in it of oil and gas. When the last edition appeared, the huge increases in the price of oil had only just begun to affect the world economy, and the need for change and for greater emphasis on efficient energy conservation was only just being recognized. Eleven years ago, the United Kingdom's own North Sea oil development was only just coming into fruition. Today, Britain is among the top six largest oil producers in the world.

At this time of rapid change in the oil industry, 'Modern Petroleum Technology' provides, in two volumes, an excellent handbook for specialists and non-specialists alike. It provides a quick reference to most aspects of the technology of the oil industry and I warmly commend it.



PETER WALKER
(Secretary of State for Energy)
London, 1984

THE INSTITUTE OF PETROLEUM

The Institute of Petroleum, a scientific society, originally known as the Institution of Petroleum Technologists, was formed in 1913.

The objectives of the Institute are:

To give objective consideration to the science, technology and economics of petroleum and its products and their uses, to express an informed viewpoint on such matters as well as to provide a forum for discussion and the exchange of ideas.

To disseminate expertise between its own committees, between the Institute and other organizations and with appropriate government departments.

To promote a flow of information of a factual nature about the science, technology and economics of petroleum and, in this connection, about the work of the Institute and the petroleum industry.

To provide appropriate services to members, both individual and collective, including opportunities for individual members to meet socially.

These objectives are met through a structure of technical committees, through publications and information services and by a network of branches.

THE IP'S ROLE: For 70 years the Institute of Petroleum has provided an impartial forum for the discussion of technical aspects of petroleum. Specialized committees cover a wide range of subjects. These include education, energy economics, engineering, exploration and production, health and safety, measurement, research, standardization, and the prevention of pollution. Codes of practice, measurement tables, standards and proceedings of symposia are produced and published. *Petroleum Review*, the Institute's informative and readable magazine, is despatched to members each month. In addition to the excellent Library, the Institute has an Information Department. Conferences and Seminars are also arranged.

MEMBERSHIP: The three categories of membership are: Student Member (S.Inst.Pet), from the age of 18 to 25*; Member (M.Inst.Pet), who should be not less than 21 years of age; and Fellow (F.Inst.Pet.). A Fellow must have been a Member for not less than 5 years, must satisfy Council that he has appropriate professional, technical, scientific or academic qualifications and have held a position of responsibility concerned with petroleum for not less than five years. An organization, such as a company, may become a collective member and may nominate a representative who is entitled to all the privileges of an individual member, except that he may not serve on Council or use an abbreviated membership designation.

BRANCHES: In addition to the thirteen branches of the IP in the United Kingdom, there are three overseas branches in Ireland, Kuwait and Singapore.

THE INSTITUTE'S TECHNICAL WORK: There are ten main technical committees, some of which have sub-committees, panels and working groups.

* Proposals to raise this upper age limit are in hand.

They have a total membership of over 1000 experts in the various fields, primarily from the oil industry, but also from government departments and other bodies. They are supported by the qualified members of the technical department of the Institute.

THE INSTITUTE'S INFORMATION ACTIVITIES: Standard technical works used internationally by the petroleum industry and allied bodies, as well as reports on IP conferences and symposia, are published each year.

Technical papers, data sheets and booklets on oil industry subjects are produced regularly.

The IP's magazine, *Petroleum Review*, has a wider circulation than the IP membership and is an informative and topical oil industry journal, dealing in depth with subjects of wide interest.

The Library and Information Departments deal with an increasing number of enquiries from members and the general public, by telephone, by mail and in person. These are well in excess of 11,000 a year. In 1981, the Library, which has 15,000 volumes, added on-line information searching to its facilities, which links the IP to 150 important data bases, mainly in North America.

The conferences organized each year by the IP include a wide range of technical and economics subjects, and range from half-day to residential conferences. The branches have their own lectures and social programmes.

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The Production of Petroleum Chemical Intermediates

By D. J. HADLEY, E. G. HANCOCK, and L. TURNER

ALONGSIDE the petroleum industry, of which the main business is the production of hydrocarbon fuels and lubricants, there has grown up what has come to be known as the petroleum chemicals industry, which defies brief and precise definition, and is perhaps best thought of as the industry that is concerned with the large-scale production of pure organic compounds. The basis of this industry is an assured and abundant supply of the simpler hydrocarbons. These were, at first, derived incidentally from natural gas or oil during the refining operations, but as the manufacture of petroleum chemicals developed special operations had to be introduced to provide enough of the various feedstocks of the requisite purity. The hydrocarbons are converted by one or more chemical reactions into consumer commodities or other saleable end-products. However, the distinction that is sometimes drawn between hydrocarbons on the one hand and petroleum chemicals or chemical intermediates on the other is quite arbitrary and may be misleading. Hydrocarbons are really the primary intermediates, and they may be converted directly into end-products (e.g. ethylene to polyethylene) or they may be transformed by a series of chemical reactions involving additional reagents and the production of other intermediates. In this chapter the main purpose is to survey the production of both the hydrocarbons and the further intermediates derived from them.

The production and chemical processing of hydrocarbon intermediates is now a very extensive and intricate subject from both the technological and the economic aspects, comparable indeed with the petroleum industry itself. Our survey, therefore, will be necessarily superficial and confined to some of the more important processes.

We shall do no more than indicate the end-products. These may, for the most part, be placed in the following groups.

Plastics and resins—Moulded, extruded, machined, and reticulated articles and materials used in the home and in the building, engineering, automobile, aviation, electric, and electronic industries, increasingly as replacements for metal, glass, leather, and other more traditional materials. Paints and surface coatings generally. Films and packaging materials. Foam for insulation and furniture.

Synthetic fibres—Clothing, floor coverings, decorative textiles, tyre cords, ropes.

Synthetic rubber—Supplements and replaces natural rubber in all its applications. Special purpose types, such as oil-resistant synthetic rubber, used for hoses, gaskets, engine mountings, etc.

Materials for agriculture—Fertilizers, cattle feed improvers, pesticides, etc.

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Cleaning agents—Detergents replace and, in some circumstances, are superior to soap. Chlorinated hydrocarbons are used for dry cleaning and degreasing, mainly in the engineering industry.

There are many other smaller outlets for petrochemicals, but already it will be evident that there are few material markets into which they have not penetrated. An incipient attack on the most important of all, the food market, is indicated by the construction of plants in which protein will be made from hydrocarbons.

Plants for the manufacture of individual hydrocarbons or petroleum chemicals rarely have a capacity of less than 5000 tons/year. A typical capacity is 50 000 tons/year. Ethylene is produced on a considerably larger scale (over 400 000 tons/year). Considering the scale of production the characteristic high purity of the chief hydrocarbons and petroleum chemicals is remarkable. Petrochemical phenol, for example, normally contains less than 0.02% wt of impurity. Other characteristics of the manufacture of petroleum chemicals are, first, the stoichiometric simplicity of the chemical reactions involved and, secondly, the use of cheap and abundant reagents for reaction with the hydrocarbon feedstocks; the most commonly employed reactants are air and water.

Petroleum chemicals represent only a small fraction of all the petroleum that is refined, but their value, weight for weight, is never less than twice and may be more than ten times that of the original hydrocarbon feedstocks.

The techniques used in their production, such as reactor design, distillation, extraction, and other methods of separation, have been largely adopted from refinery practice. Petroleum chemical plants are, however, frequently more complex than the refinery units.

This chapter consists of three sections. In the first the main petroleum sources of petroleum chemical intermediates are briefly described. In the second the manufacture of hydrocarbon intermediates is dealt with. Finally, an account is given of the principal derivatives of hydrocarbons.

SOURCES OF PETROLEUM CHEMICAL HYDROCARBONS

All petroleum chemical installations must have ready access to the various refinery fractions used as raw materials, and it is natural that such installations are placed on the same site as, or closely adjacent to, an oil refinery. Close integration of the two sides of the industry (it is nowadays unrealistic to consider them as separate industries) is further demanded by the fact that certain by-products from the chemicals operation (e.g. steam-cracked gasoline) are in part returned to the refinery. In accordance with the above situation, it will be seen in the following section that the petroleum chemicals industry can call upon a variety of feedstocks, including natural gas and straight-run oil fractions, as well as lesser amounts of feedstocks derived from refinery processes.

Petroleum Gases

Naturally-occurring gas (see next chapter) is an important source of methane, ethane, propane, butanes, especially in the USA, Eastern Europe, and USSR.

Natural gas is the term used to designate methane-rich material, whilst the C_3–C_4 fraction (usually handled after liquefaction by pressure) is called LPG (liquefied petroleum gas)—see also next paragraph. The term 'natural gas liquids' is also used to cover all the condensable liquid hydrocarbons from natural gas. A gas mixture containing substantially ethane has long been used as a cracking feedstock in USA and plants are now being erected in Europe. Very high yields of ethylene are obtained but only small quantities of higher olefins.

Liquefied Petroleum Gas

Certain refinery processes produce mixtures of gaseous hydrocarbons in sufficient quantity to be useful as feedstocks for the petroleum chemicals industry—see Chapters 14, 15 and 18. The condensable C_3–C_4 fraction of such gases is designated LPG. There are three processes which give rise to important quantities of LPG: catalytic cracking, catalytic reforming, and hydrocracking. Catalytic cracking yields propane, propylene, butanes, and butenes (but not butadiene). The olefins can be used directly as chemical feedstocks, after separation of the C_3 and C_4 fractions. Catalytic reforming and hydrocracking yield butanes (high iso/n ratio), propane, and ethane (relatively little from hydrocracking).

Straight-run Petroleum Liquids

Easily the most important liquid fraction of petroleum for the petroleum chemicals industry is naphtha which is a light distillate feedstock (LDF), typically a C_5 to 160 °C cut, which in Europe and Japan is almost the exclusive feedstock for steam-crackers, producing hydrogen, methane, ethylene, propylene, the butenes, butadiene, and to a lesser extent benzene and isoprene.

Kerosine and gas oil are used for the extraction of C_{10}–C_{13}, and C_{14}–C_{18} n-paraffins, respectively. Gas oil has, to a very limited extent, been used in place of naphtha as a steam-cracker feed, yielding similar products but in a different ratio.

Paraffin wax of approximate carbon number range C_{25}–C_{30} is a source of valuable C_6–C_{20} linear α-olefins via steam-cracking.

Finally, a number of processes for the production of lower hydrocarbons by the thermal cracking of crude oil itself are at varying stages of development, some at almost commercial level.

Products from Cracking and Reforming

As well as straight-run materials, certain liquid-hydrocarbon streams from refinery processes serve as a source of hydrocarbons for the chemical industry. Only three are of importance: a C_5 cut from catalytic cracking, a naphtha-range fraction from hydrocracking, and a C_6–C_8 cut from catalytic reforming. For the derivation of these, see Chapters 14 and 15.

Catalytic cracking yields a liquid, the C_5 cut of which is a valuable source of isopentenes (isoamylenes) which may be subsequently dehydrogenated to isoprene.

Catalytic reforming of straight-run material yields a C_6–C_8 reformate rich in the aromatic hydrocarbons, benzene, toluene, ethylbenzene, and the xylenes. The raffinate remaining after recovery of the aromatic hydrocarbons is sometimes used to augment straight-run naphtha as a steam-cracker feedstock.

Naphtha-range products from the hydrocracking of heavier oil fractions are also very occasionally used as steam-cracker feedstocks.

A complete list of the sources of petroleum chemical hydrocarbons is given in Tables I(*a*) to I(*d*).

TABLE I(*a*)

Sources of Naturally-Occurring Hydrocarbons Used as Petroleum Chemicals Feedstocks

Source	Hydrocarbon
Natural gas	Methane with traces of ethane, propane, and butanes
Natural gas liquids	Ethane, propane, butanes, etc.
Liquid petroleum gas	Propane, butanes
Naphtha	C_4–C_{12} hydrocarbons
Kerosine	C_9–C_{16} hydrocarbons
Gas oil	C_{15}–C_{25} hydrocarbons

TABLE I(*b*)

Petroleum-Chemical Hydrocarbon Intermediates from Refinery Processes

Process	Hydrocarbon
Catalytic reforming of naphtha	Propane, butanes, benzene, toluene, xylenes, ethylbenzene
Hydrocracking of heavy straight-run fractions	Propane, butanes
Catalytic cracking of heavy straight-run fractions	Propane, propylene, butanes, n- and iso-butenes, isopentenes

TABLE I(*c*)

Petroleum-Chemical Hydrocarbon Intermediates from Non-Refinery Cracking Processes

Process	Products
Steam cracking of NGL, LPG, naphtha or gas oil	Ethylene, propylene, n- and iso-butenes, butadiene, C_5 olefins, benzene, toluene, and xylene
Partial combustion of methane or light naphtha	Acetylene, ethylene
Arc cracking of methane, LOG or LDF	Acetylene, ethylene
Regenerative cracking of C_3–C_4 alkanes or naphtha	Acetylene, ethylene
Steam-cracking of a C_{25-30} wax	Linear C_{6-20} alpha-olefins
Steam-cracking of 2-methylpentene-2	Isoprene

TABLE I(*d*)
Petroleum-Chemical Hydrocarbon Intermediates by Various Processes

Process	Products
Dehydrogenation	
of n-butane	n-Butenes, butadiene
of n-butenes	Butadiene
of isopentenes	Isoprene
of ethylbenzene	Styrene
Hydrogenation	
of benzene	Cyclohexane
Alkylation	
of benzene with ethylene	Ethylbenzene
of benzene with propylene	Cumene
of benzene with propylene tetramer	Dodecylbenzene
De-alkylation	
of toluene or steam-cracked gasoline	Benzene
Dimerization, trimerization, etc.	
ethylene oligomerization	Linear C_{6-20} alpha-olefins
propylene dimerization	Methylpentenes
propylene oligomerization	Nonenes Propylene tetramer
propylene/butenes oligomerization	Mixed heptenes
isobutene oligomerization	Di- and tri-isobutene
Disproportionation	
of propylene	Ethylene plus n-butenes
of toluene	Benzene plus xylenes

PRODUCTION OF INDIVIDUAL HYDROCARBONS

Acetylene

All processes for producing acetylene from petroleum liquids and gases are high energy consumers and have not proved very viable except where cheap power was available. Further, during the last twenty years processes have been developed for producing most of the chemicals, which hitherto, had been considered an acetylene preserve, from ethylene or propylene. New plants are therefore unlikely to be erected in the foreseeable future.

Much acetylene in many countries is still being produced by the older carbide (non-petrochemical) route. This can be carried out in small units and is largely used in acetylene welding, etc.

While there are many processes for the production of acetylene from petroleum hydrocarbons it is fair to say that the essential operation is to heat the hydrocarbon to a very high temperature followed by rapid quenching and a very complex separation process. Probably the process which has been most widely commercialized is that developed by BASF, based on the partial oxidation of natural gas or methane from other sources. The heat produced in the partial oxidation raises the temperature of the remainder to about 1500°C when the methane cracks, mainly to acetylene and hydrogen. The former, however, at this temperature is thermodynamically unstable and partly reverts to methane or reacts with itself or with other by-products of the original

reaction to form a wide range of compounds. It is essential, therefore, to cool the gas stream as rapidly as possible and naphthalene is the preferred medium for this operation. The separation of the acetylene is essentially carried out by absorption in a solvent such as n-methyl pyrrolidone. This separates off the CO and CO_2 produced in the partial oxidation as well as the less reactive hydrocarbons. Hydrocarbons which dissolve must be removed by a pre-scrubbing treatment with oil, or by partial preliminary stripping of the acetylene-rich solvent. The last traces of CO_2 are removed by washing the acetylene with caustic soda. The yield of acetylene on hydrocarbon raw materials is only of the order of 8–10 per cent. The above is only the barest outline of a process which is very complicated. A diagram of the BASF process is shown in Fig. 1.

Numerous other processes have been developed with limited success. Hüls

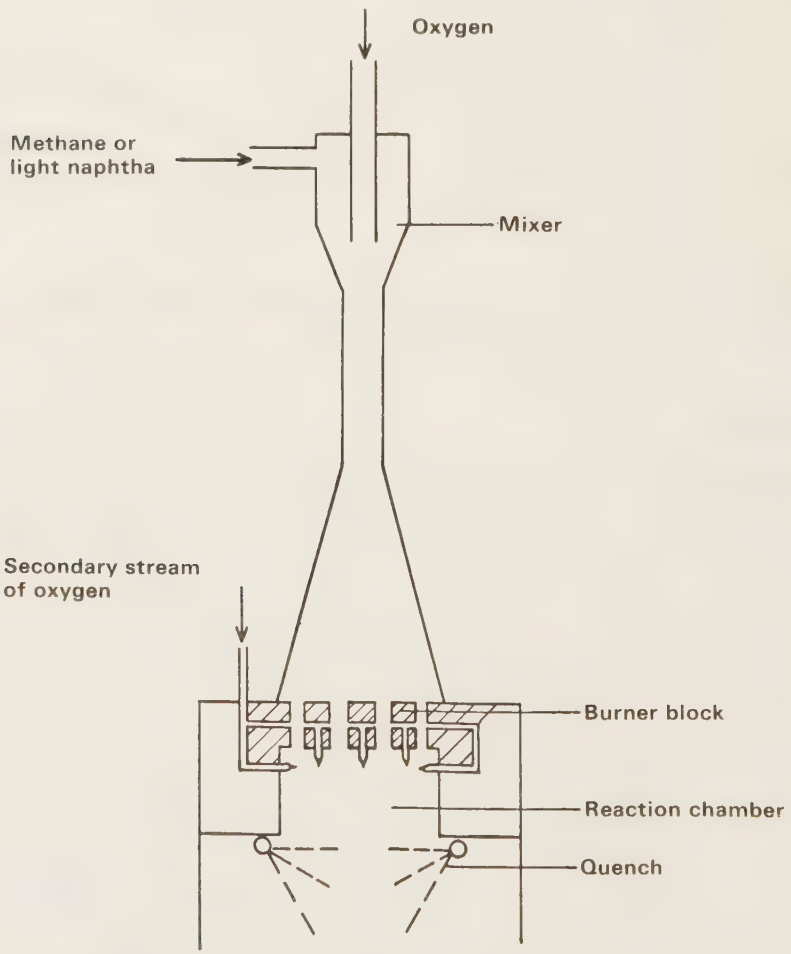


FIG. 1. BASF burner for flame cracking of hydrocarbons to acetylene. (Courtesy of Dr H. Friz, BASF.)

developed a process which uses an electric arc (and not partial combustion) to obtain the required temperature. The Wulff process uses the heat developed by combustion of the by-products and a regenerative furnace. Steam is injected with the feedstock and a combined pressure of 0.5 atm and a temperature of 1500°C for a period of 0.3 sec. Up to 14 per cent of acetylene is produced. Quenching and separation are basically similar to the BASF process. By use of less drastic conditions ethylene can be produced as a co-product and this has been made use of in the production of vinyl chloride (see below). While the above processes function most simply on methane, liquid hydrocarbons including naphtha have been used but, again, only with limited success.

Ethylene

Steam-cracking of naphtha, etc.

This is by far the most important source of C_2–C_5 petroleum chemicals intermediates in Western Europe and Japan. Hydrocrackates or catalytic reformates boiling in the naphtha range are used in a very few locations to augment the straight-run material. Propylene, the butenes, and butadiene are gaseous co-products of ethylene, and their manufacture by steam-cracking is inevitably dealt with here—reference back to this section is made in later sections dealing with the individual hydrocarbons.

It should be explained that steam cracking is the only type of cracking dealt with in this chapter and is virtually the only one used for the specific production of petrochemicals from petroleum raw materials. The use of non-steam cracking for second-stage products is, however, included. All other types of cracking of petroleum fractions are dealt with in Chapter 14, even though these processes do produce some petrochemicals or petrochemical feedstocks as by-products.

The advantages of using steam are that the formation of coke is minimized and the partial pressure of naphtha or other feedstock is reduced, thus increasing the yield of gaseous as distinct from liquid products.

The production of ethylene as a base material for petrochemicals has increased enormously over the years and is now estimated to be of the order of 30 MM tons world-wide.

There are four basic petroleum raw materials from which ethylene can be produced: ethane, LPG, naphtha, and gas oil. Which of the four to choose depends upon their availability, and hence cost, and on the products desired. Except in the case of ethane, where their production is minimal, other gaseous products, mainly C_3 and C_4 olefins are produced along with the ethylene, and these are normally valuable in their own right. Some methane and hydrogen are produced as by-products along with smaller quantities of other paraffin hydrocarbons. By choosing the right conditions a considerable quantity of a gasoline-like liquid is produced which is high in aromatics.

A great deal of ethane, about 47 per cent of the total petroleum raw material, is used in the States, but in Europe and Japan naphtha has been the preferred raw material, mainly because until quite recently supplies of cheap ethane did not exist. During the 1970s there was a move towards the use of gas oil as it was feared that supplies of naphtha might be insufficient. The world recession

TABLE II
Steam Cracking Yields from Various Raw Materials

	Ethane	LPG	Naphtha	Gas oil
Ethylene	80.5	40	32	25
Propylene	2	16	15	15
Butadiene	1	1.5	4.5	4.5
Butenes	neg.	neg.	4.5	5
Liquid products	1.5	10	25	37

having reduced the demand for gasoline as well as of some petrochemicals, it has followed that naphtha is once more in free supply.

LPG has been less used even though it can give an excellent range of products. The main reason for this is that LPG has such a large market as a domestic and industrial fuel. Some 10 per cent has been used in the States.

The yields from the various raw materials expressed as a percentage by weight of the feedstock under average cracking conditions are given in Table II.

The remainder is made up of by-products as described above. Some coke may also be produced, and traces of acetylene-type compounds and a little hydrogen sulphide from sulphur existing in the raw material.

The figures in Table II are only approximate; they can vary widely according to the conditions of steam cracking and to the exact composition of the raw material. Thus any appreciable quantity of isobutane in the LPG will significantly reduce the ethylene yield. Naphthenes in the naphtha do not crack so readily and increase the proportion of butadiene, again at the expense of the ethylene, while isoparaffins as distinct from n-paraffins increase the yield of propylene. Aromatics in the naphtha are little cracked and appear in the liquid products in a concentrated form. The effect of cracking naphthas of differing compositions is also shown in Table III. The effect of the severity of the steam cracking is shown in Table IV.

In general, nowadays, low/medium severity crackers give 15 to 20 per cent of ethylene, and they have some flexibility in ethylene/propylene ratio (about 1.0 to 1.4), but specially-designed high-severity furnaces are required for ethylene yields in the 30 per cent region (ethylene/propylene ratio of 2.0 or more).

TABLE III
Comparison of Yields from Paraffinic and Naphthenic Type Naphthas

Composition of naphtha (%)		
Paraffins	69	44.3
Naphthenes	21.8	43.3
Aromatics	8.3	12.4
Distillation range °C	42–184	46–177
Products, percentage of feedstock		
Ethylene	28.6	22.3
Propylene	14.1	14.3
Butadiene	3.5	5.5

TABLE IV
Steam-Cracking Yields from a Typical Middle East Naphtha

Severity	Low	Medium	High
Products, % wt on feed:			
Hydrogen	0.50	0.54	0.95
Methane	10.1	12.0	15.0
Ethylene	15.0	19.2	30.7
Propylene	14.8	16.6	12.3
Isobutene	3.2	2.9	1.5
Butadiene	2.5	3.3	4.1
Gasoline	36.3	30.0	24.9
Rest to 100			

The product distribution from steam-cracking can be varied, within limits, according to choice of feedstock (e.g. crude source and boiling-range of straight-run naphtha) and the severity of operation, the latter being controlled by variation of temperature and residence time in the cracking zone. Broadly speaking, feeds rich in n-paraffins (e.g. from Kuwait crudes) give the highest ethylene yields, those rich in naphthenes (e.g. from Nigerian crudes) give less ethylene and more butadiene.

Although the principles of steam cracking do not vary greatly according to the raw material used some difference in the design of plants is necessary to cope with a gas like ethane or a liquid like naphtha. With regard to gas oil some multi-purpose plants have been constructed to use either naphtha or gas oil; such plants do result in some overall reduction in efficiency.

In the next section the operation of plants based on ethane or LPG and on naphtha will be described in outline:

(1) From ethane (or LPG)

(a) The liquid ethane from the separation process is vaporized and scrubbed with an amine to remove any carbon dioxide.

(b) It is then combined with recycled ethane, preheated with the quench water, and sent to the cracker heaters.

(c) The ethane is cracked in tubular heaters at just under 900°C in the presence of dilution steam.

(d) The gases are cooled by the quench water, and the condensed steam allowed to overflow from the quench tower and the gases compressed.

(e) The compressed gases are scrubbed with caustic soda to remove any acid gases, cooled, and dried by activated alumina.

(f) The gas is progressively chilled and partly condensed. This is done with ethylene and propylene refrigeration systems and also by vaporizing recycled ethane.

(g) A hydrogen-rich gas stream is separated off and the condensed hydrocarbons fed to the distillation train.

(h) The condensate is then separated into its components by distillation according to usual ethylene practice.

2) From naphtha or gas oil.

The feedstock is vaporized, steam added in a ratio of about 0.3–0.5 tonne of steam per tonne of naphtha, and the two heated rapidly to the cracking temperature through tubular coils inside an oil- or gas-fired furnace. Alternatively, the furnace may consist of four parallel tubes through which the naphtha and steam pass downwards countercurrent to the upward flow of combustion gases. A typical furnace of the latter type is the Stone and Webster furnace shown diagrammatically in Fig. 2.

The temperature of operation varies from 750 °C for medium/low severity to 900 °C for high severity. To obtain the best yield of ethylene an important factor is a very short residence time, e.g. 0.25 sec, this particularly reducing the amount of coke produced. Longer residence time, e.g. 0.6 sec at low/medium severity increases the yield of aromatics.

Using gas oil the cracking temperature should not be above 820 °C, while the steam ratio must be much higher, e.g. tonne for tonne and the residence time kept very short.

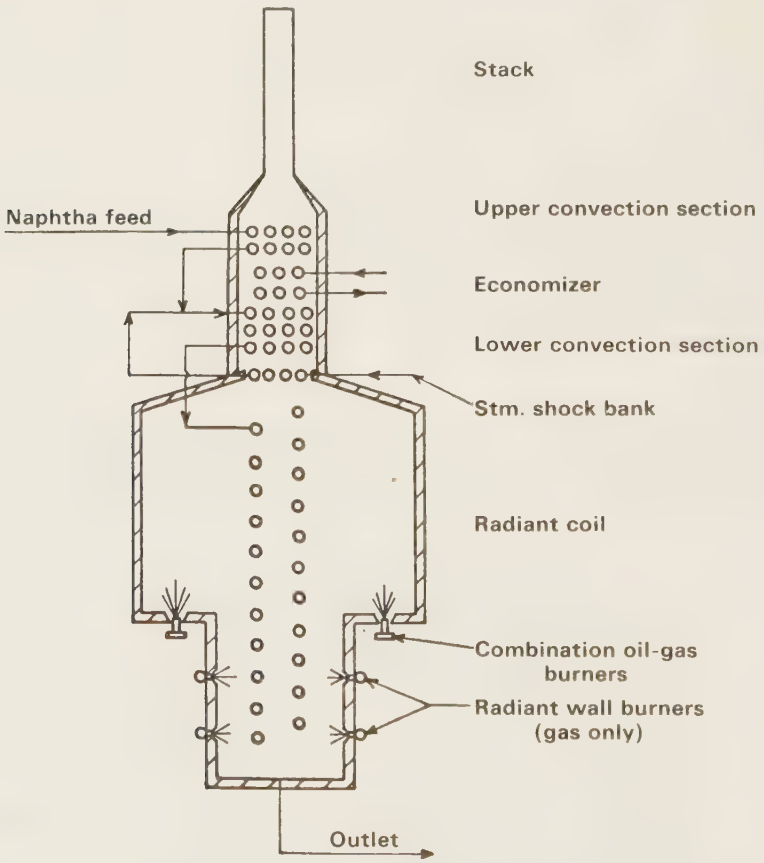


FIG. 2. Schematic diagram of Stone and Webster cracking furnace. (Courtesy of *Hydrocarbon Processing*.)

While it was explained earlier that this section would be confined to steam-cracking it must be mentioned that an interesting development known as hydropyrolysis is taking place. This uses high pressure hydrogen to break down both heavy and light petroleum feedstocks. Hydrogen helps to inhibit the formation of both coke and heavy oil products. By recycling the saturated hydrocarbons yields of ethylene up to 40 per cent of the feedstock can be obtained, combined with a marked saving in energy costs. The high cost of hydrogen is the main drawback.

A process based on the steam cracking of crude oil has been developed by Kureka in Japan. Very high temperatures are required, e.g. 2000°C, but few details are known.

Separation of the olefins

This is an outline of the process used to separate the olefins when working up the products from steam cracking of naphtha.

The cracking-furnace effluent contains components with boiling points ranging from −252.7°C (hydrogen) to above 200°C (fuel oil plus tar). The normally-liquid products, i.e. of carbon number 5 or more, are first separated from the gases. The gases are then compressed and fractionally distilled at low temperatures, and the liquid is split into raw steam-cracked gasoline (typically C_5–200°C) and fuel oil plus tar.

In all recovery plants the quenched furnace effluent is further cooled by direct oil injection and the combined stream is then led to the primary fractionator (see Fig. 3) where steam-cracked gasoline, lower hydrocarbons,

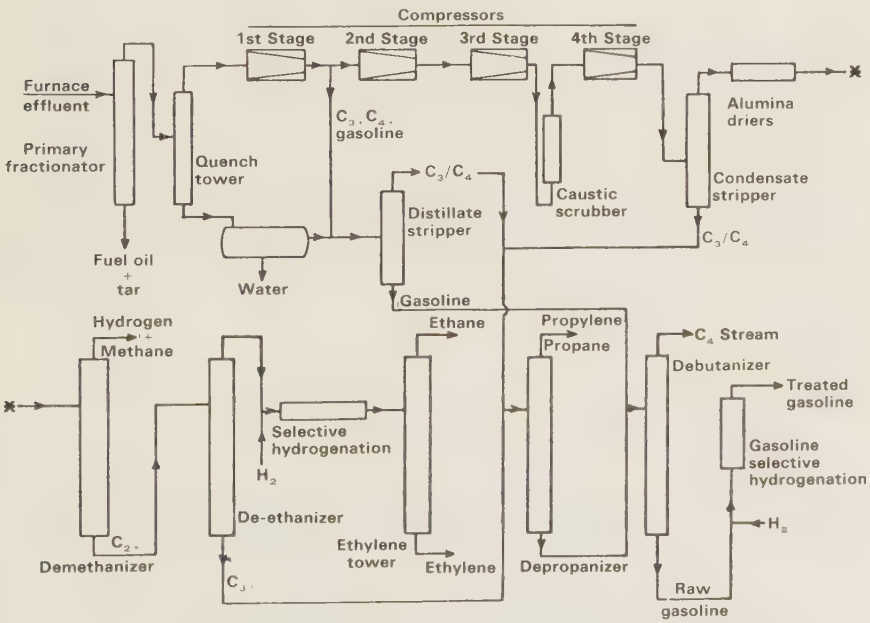


FIG. 3. Simplified plant diagram: recovery of steam-cracker products.

and steam pass overhead, and fuel oil plus tar are taken as bottoms. The overhead stream is cooled and partially condensed to give a water gasoline mixture, the components of which are separated. The cracked gasoline, which contains paraffins, olefins, dienes, and aromatics, is eventually passed with hydrogen over a catalyst (e.g. supported nickel in the BP process) which promotes the selective reduction of dienes to olefins. Because dienes are gum-formers, their removal is essential before the gasoline can be passed back to the refinery gasoline pool.

The primary fractionator comes first in all cracker recovery processes. Once the C_4 and lighter stream is separated from the heavier products, however, the subsequent separation into hydrogen, methane, ethane, ethylene, propane/propylene, and a C_4 stream is carried out in a variety of ways. Much chemical engineering ingenuity has gone into devising ever more efficient means of gas separation, and it is unlikely that any two plants have identical gas separation systems.

Low-pressure systems where gas streams were compressed to 12 atm and the C_3–C_4 streams separated as liquids have often been used in the past. The C_2s, methane, and hydrogen are cooled to 140°C when the C_2s are separated from the more volatile gases. More recently, however, the trend has been to use higher pressures, e.g. 35 atm and a simplified plant diagram is shown in Fig. 3.

Cracked gas is compressed to 35 atm in four stages, most of the remaining gasoline (C_{5+}) being removed as liquid after the first stage. Following the third stage, H_2S and CO_2 are removed by caustic scrubbing. After the fourth stage some C_3 and C_4 are removed as liquid, and the gas is dried by alumina so that neither ice nor solid gas-hydrates form in the distillation towers. The dry gas is cooled to −80°C by successive exchange with liquid propylene and then ethylene, and passes to the demethanizer column which gives residue gas (hydrogen plus methane) as overheads, and a liquid C_2–C_4 stream as bottoms. This passes to a de-ethanizer column which separates liquid ethylene/ethane overhead from a C_3–C_4 stream at the base. The C_2 stream is vaporized and is selectively hydrogenated for the reduction of acetylene (typically 0.8 per cent of the C_2 stream) to ethylene. The effluent is cooled and re-condensed before entering the ethylene tower in which ethane and ethylene are separated. The de-ethanizer bottoms, combined with the C_3 C_4 stream separated after the fourth stage compression, are passed successively to columns which separate a C_3 stream (which may also require selective hydrogenation to remove propadiene and methylacetylene) and a C_4 stream, thus completing the separation of the main products.

Minor sources of ethylene

The co-production of ethylene with acetylene has been mentioned in the section on the latter.

One or two plants are operating on a process for converting propylene into ethylene plus n-butenes via disproportionation (Phillips Petroleum Co.):

$$2C_3H_6 \longrightarrow C_2H_4 + C_4H_8$$

This reaction is catalysed by cobalt plus molybdenum oxides on alumina, or alternatively by tungsten oxide on silica. It is attractive economically only

when a high value can be placed on the n-butenes, e.g. as a butadiene source in the USA.

Propylene

The manufacture of propylene by steam-cracking has been dealt with above, under ethylene. In the USA, and to a lesser extent elsewhere, propylene is also isolated from the products of catalytic cracking. Conventional low-temperature distillation is used to separate the C_3 fraction from C_2 and C_4, and if necessary the propane and propylene can be similarly split.

Through reaction of the C_3 stream with sulphuric acid propylene and any propane can be separated, the propylene forming isopropyl alcohol (see below).

The C_4 Olefins and Diolefins

Butadiene $CH_2{=}CH{-}CH{=}CH_2$

There are three routes of industrial significance to this important diolefin. In Europe and Japan it is obtained mainly by extraction from the C_4 stream produced by naphtha cracking. Butane or butenes dehydrogenation accounts for most of the butadiene produced in the USA. In the USSR some butadiene is still made by a direct route from ethanol though the route involving the extraction of butadiene from the C_4 stream from a steam cracker is gaining ground.

Butadiene from Naphtha Cracking

The recovery of the C_4 fraction from this process has been described under ethylene, above. The yield of C_4 hydrocarbons based on naphtha fed is usually 8–12% wt, of typical composition:

C_3 3, butanes 7, n-butenes 27, isobutene 34, butadiene 29% wt

The yield and composition vary with the feedstock and with cracking severity.

Simple fractional distillation will not suffice to yield a pure butadiene, as Table V shows.

TABLE V
Boiling Points of C_4 Hydrocarbons

C_4	bp °C
Isobutane	−11.7
Isobutene	−6.9
Butene-1	−6.3
Butadiene	−4.4
n-Butane	−0.5
trans-Butene-2	0.9
cis-Butene-2	3.6

Butadiene is recovered from such streams by extraction with a selective solvent, of which a number are in use.

(1) Countercurrent extraction of the liquefied C_4 fraction with aqueous cuprammonium acetate is an early, cheap process which is now being steadily displaced by extractive distillation processes based on organic solvents. These processes are somewhat more expensive, but give a product meeting today's more stringent purity specifications.

(2) Several organic solvents have been found to have a good selectivity for butadiene present in C_4 streams. Roughly in order of historical development the solvents used are: furfural, acetonitrile, dimethylacetamide, dimethylformamide, and N-methylpyrrolidone. The processes are rather similar technically, and the choice between them is nowadays mainly on economic grounds. The Shell acetonitrile process will be given in a simplified form as typical of such processes (Fig. 4).

The feed is depropanized to remove C_3 hydrocarbons, and the C_4 bottoms product is pumped to near the top of the extraction column where it meets a solution of water (15 per cent) in acetonitrile at about 130°C under pressure. The butadiene dissolves in the solvent along with a small amount of butenes and minor impurities, and leaves the tower as bottoms product. Most of the butenes and butanes are removed as overhead reflux, and are water-washed in a further column to recover acetonitrile before leaving the plant.

The butadiene-rich solvent is sent to the butadiene stripper column where

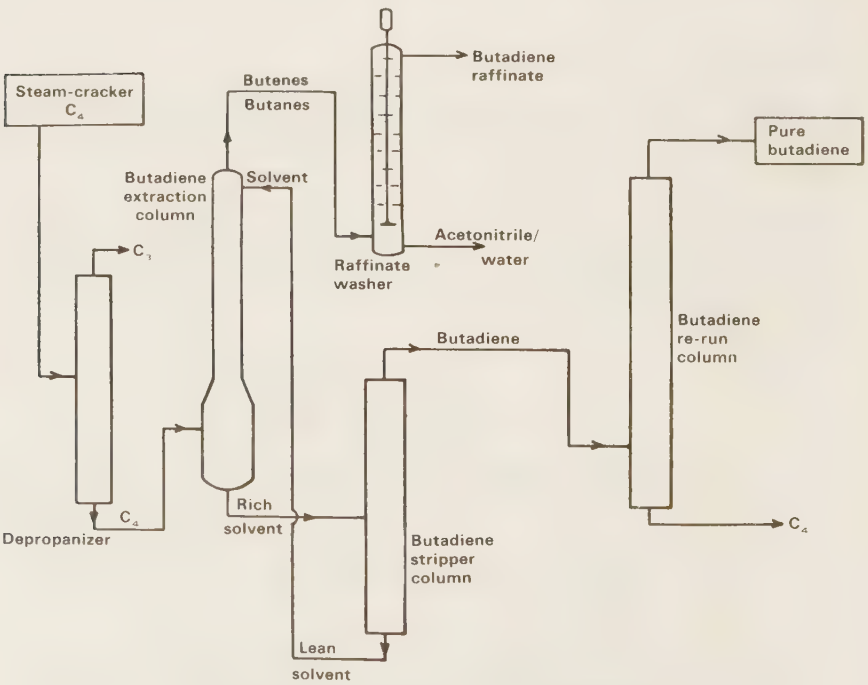


FIG. 4. Butadiene recovery by acetonitrile extraction.

the pressure is lowered somewhat and butadiene passes overhead, whilst the lean solvent passes out at the bottom and is pumped back to the extraction tower. The butadiene is rerun in a separate distillation column which removes butenes and small amounts of acetylenes as base product, and yields pure butadiene overhead. This may require caustic washing to remove traces of acid. A small amount of polymerization inhibitor is added, and the butadiene is sent to storage.

Butadiene by butane or butenes dehydrogenation

These processes were rapidly developed in the USA in the early 1940s to provide a source of synthetic rubber (of which butadiene is a component) after the entry of Japan into the war had cut off supplies of natural rubber. As now, the feedstocks then available were:

n-butane, separated from isobutane by fractional distillation of the C_4 fraction of LNG or LPG, and

n-butenes, from cat. cracker C_4 streams of typical composition: C_3 2, isobutane 22, n-butane 20, n-butenes 29, isobutene 25, C_{5+}, 2, % wt.

Isobutene is first recovered by acid extraction or is directly converted into polyisobutenes, and the n-butenes are then separated from the butanes by extractive distillation with acetonitrile, acetone, or furfural.

(*a*) *n-Butane dehydrogenation*

This was first practised in the USA during the Second World War, as a two-stage route based on processes developed by Esso/Shell and by Phillips. Houdry later developed a one-stage route which proved successful enough to preclude the erection of further two-stage plants, and the Houdry process will be described in some detail below.

Butane dehydrogenation involves a series of equilibria:

$$CH_3CH_2CH_2CH_3 \rightleftharpoons H_2 + \begin{matrix} CH_2{=}CHCH_2CH_3 \\ CH_3CH{=}CHCH_3 \\ \text{(cis and trans)} \end{matrix} \rightleftharpoons H_2 + CH_2{=}CHCH{=}CH_2$$

Although at 600 °C and 0.167 atm the equilibrium mixture contains: n-butane 8, n-butenes 64.5, butadiene 27.5% wt, corresponding to a 92 per cent conversion of butane, in practice the conversion of n-butane present in the reactor feed (57 per cent) is held to about 35 per cent, and unconverted butane and butenes are recycled.

The forward reactions in the above series are all endothermic and are therefore carried out at as high a temperature as possible, limited in practice to 650 °C to avoid excessive cracking and coking on the chromium oxide/alumina catalyst used. The increase in volume accompanying dehydrogenation means that the equilibria are displaced towards butadiene at reduced pressures, the use of which also serves to minimize cracking and coke formation.

The above facts dictate the main outlines of the Houdry process, which is represented in a simplified form in Fig. 5.

Fresh n-butane, plus a recycle stream containing n-butane and n-butenes, enters one of three fixed-bed catalytic reactors charged with chromia-alumina, at 600–650°C and 3–4 psia pressure. After a reaction cycle of about 7 min the feed is switched to another reactor. The first reactor is purged to recover products, and then air is blown in to burn off coke from the catalyst and so raise its temperature to 600–650°C again (purge and regeneration cycle). The third cycle in the reactor involves evacuation to reaction pressure. When this has been reached the series of cycles is repeated. The other two reactors are synchronized with the first to give a continuous overall process.

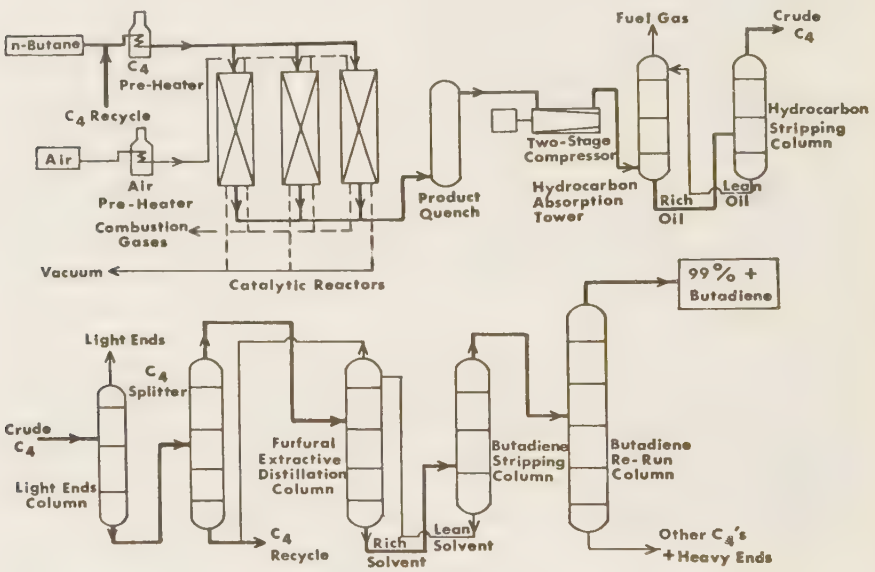


FIG. 5. Butadiene by dehydrogenation of butane: Houdry process.

The reactor effluent is quenched, compressed, and then scrubbed with oil to absorb C_4 and some lighter hydrocarbons, leaving an off-gas containing hydrogen, methane, and some heavier materials, which serves as fuel gas. The rich oil is stripped and the gases are passed to a light ends column for removal of C_3 and lighter materials overhead. The bottoms C_4 stream is split by fractional distillation into isobutane, isobutene, butene-1 and butadiene overhead, and n-butane plus the butenes-2 as bottoms (recycled).

From the overheads, butadiene is recovered by extractive distillation with a 4 per cent solution of water in furfural, the butadiene-rich solvent passing to a stripper column where the diene is taken overhead. A final butadiene rerun column serves to remove heavy polymer, butene-2, 1,2-butadiene, and acetylenes, yielding a final product of purity approaching 99 per cent. The C_4s not absorbed in furfural are recycled.

(b) n-Butenes dehydrogenation

The first plant for the production of butadiene from n-butenes, based on a Standard Oil process, came on-stream in the USA in 1944. The chemistry and equilibrium considerations for butenes dehydrogenation are broadly the same as those discussed above for butane dehydrogenation, and the processes are closely similar technically.

The original Standard Oil catalyst (ferric oxide supported on magnesium oxide, plus potassium and cupric oxides as promoters) has since been displaced by better catalysts developed by Shell (potassium carbonate on ferric oxide, promoted by potassium phosphate and chromium oxide), and Dow (calcium and nickel phosphates promoted by chromium oxide).

Whereas the Houdry butane dehydrogenation is operated at about 0.25 atm absolute pressure with no inert diluent, the Shell and Dow catalysts for butenes dehydrogenation are used with heavy steam dilution (about 10 and 20 vol respectively per vol of butenes) at about 1.5 to 2 atm total pressure. The steam serves not only to lower the partial pressure of the butenes, but also slows down the deposition of coke on the catalyst by removing some of it via the water–gas reaction. The Shell catalyst requires regeneration, i.e. coke burn-off, about once a week, and the Dow catalyst about once every 15 min. This is compensated economically by the fact that the selectivity and conversion are higher on the Dow catalyst:

	Dow Type B	Shell Type 205
Conversion, %	33–45	25
Selectivity to butadiene (mol per 100 mol converted)	90	75

The C_4 stream is isolated from the total dehydrogenation products by conventional fractional distillation, and the butadiene may be extracted from it by any of the processes described under butane dehydrogenation above.

Isobutene

The only significant sources of isobutene are the C_4 fraction from naphtha steam-cracking, and that from the catalytic cracking of heavy oil fractions. After the extraction of butadiene from the former, a raffinate is obtained which is qualitatively of the same composition as the cat.-cracked C_4 stream. Either stream can be used as feed to an isobutene extraction process or to a poly-isobutenes plant. The isobutene content is typically 25 per cent in a cat.-cracked C_4 stream, and 45 per cent in a butadiene raffinate from naphtha steam-cracking. Isobutene extraction is based on the selective reaction of this olefin with strong aqueous sulphuric acid, when a solution of t-butyl hydrogen sulphate and t-butanol is formed in the cold:

$$\text{i-}C_4H_8 + H_2SO_4 \rightleftharpoons \text{t-}C_4H_9SO_4H$$

$$\text{t-}C_4H_9SO_4H + H_2O \rightleftharpoons \text{t-}C_4H_9OH + H_2SO_4$$

The butanes and n-butenes are removed from the isobutene-rich acid as a separate phase, and on diluting the acid solution, and heating, the reactions shown above are reversed and isobutene is liberated.

Older processes offered by a number of contractors rely on isobutene absorption in 65 per cent sulphuric acid at 10–20°C. The C_4 stream, as a liquid phase under moderate pressure, is mixed with the acid and the mixture is passed to a series of mixer-settler tanks in which hydrocarbon and acid pass countercurrently. The undissolved hydrocarbon layer is removed, washed with water to eliminate dissolved acid, and is passed out of the plant as isobutene raffinate. The isobutene-rich acid layer is flashed to remove small amounts of absorbed hydrocarbons other than isobutene, and is then diluted to an acid strength of about 45 per cent, and heated at a lower pressure to remove the liberated olefin. This is compressed and then redistilled to remove small quantites of low polymer (polyisobutenes, and co-polymers of n- and isobutene) as bottoms, and to yield pure isobutene overhead. The diluted acid is then reconcentrated to 65 per cent before recycling.

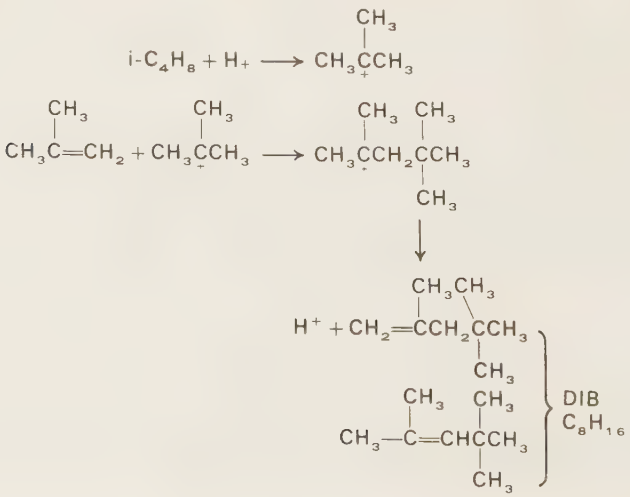
In the early 1960s the CFR (Compagnie Française de Raffinage) developed an attractive modification which avoids the expensive acid reconcentration. Absorption occurs into 50 per cent acid at ambient temperature, the isobutene-rich acid is flashed as before, and the isobutene is then removed by raising the temperature and lowering the pressure somewhat, without diluting the acid, which is merely cooled and recycled. About 90 per cent of the isobutene in the feed is recovered at a purity (after a final fractional distillation) of between 99 and 99.8 per cent. The loss as polymer is about 5 per cent on isobutene.

Because the direct conversion of isobutene, in a C_4 stream, into polyisobutenes does not involve the isolation of the olefin as an intermediate this process is not dealt with here.

Processes are now being developed using molecular sieves, the specific sieve absorbing n-butenes but excludes isobutene.

Di- and tri-Isobutylenes

If the solution of isobutene in 65 per cent sulphuric acid, mentioned above, is heated to about 90°C for 1 hour, the free olefin present in the equilibrium mixture dimerizes and trimerizes via a cationic mechanism:



The trimer ($C_{12}H_{24}$) is an isomer mixture formed from DIB and a further molecule of isobutene. The polymers appear as a separate phase, and are water washed and distilled.

The main outlets for DIB are as feedstock for the preparation of a C_9 oxo alcohol, and octyl phenols (detergent precursors); a little is also hydrogenated to 2,2,4-trimethylpentane and used as a solvent. The TIB, and a small amount of isobutene n-butenes co-dimer also formed in the process find a variety of uses. Both DIB and TIB can be put back into the motor gasoline pool.

n-Butenes

After separation of the isobutene the remaining fraction contains the n-butenes together with some n- and iso-butanes according to the source of the stream. For many reactions the butanes are not objectionable, but where pure butenes or their separate isomers are required this can be achieved by fractional distillation.

Isopentenes (Isoamylenes)

Isoprenes (2-methylbutene-1,2-methylbutene-2, and 3-methylbutene-1) occur in the C_5 fraction from the catalytic cracking of oil fractions (see Chapter 14). The isopentene content is typically 25–45 per cent, with 2-methylbutene-2 by far the predominant isomer.

In the Sinclair recovery process the feed, in the liquid phase, is contacted with 65 per cent sulphuric acid at about 20°C when 2MB2 and 2MB1 are extracted. The isopentene-rich acid, after removal of the separate layer of undissolved hydrocarbons, is warmed to about 37°C in the presence of a solvent consisting of C_6–C_{10} paraffinic hydrocarbons which dissolves the isopentenes ejected from the acid solution. The two phases are separated, and the acid is recycled—note that no reconcentration is required. The rich-solvent phase is caustic washed to remove acid, and is then distilled to recover the isopentenes from the solvent. During the second stage, in which the rich-acid solution is warmed, some 3 per cent of the isopentenes polymerizes, and some of the recovered solvent is therefore purged to avoid polymer build-up. Typical feed and product analyses are given below:

	% wt	
	Feed	Product
C_4	0.9	0
Isopentane	25.9	0.5
n-Pentane	7.6	0.2
Pentene-1	5.1	0.1
Pentene-2	18.6	0.3
Isopentenes	41.3	98.9
C_{6+}	0.6	0
	100.0	100.0

The only outlet for isopentenes at present is in isoprene manufacture.

Isoprene

This is only present to a small extent in the C_5 fraction from naphtha cracking, but a slightly impure product can be obtained by an extractive distillation with acetonitrile in a process broadly similar to that described under butadiene.

There are two processes of industrial importance for producing isoprene: the dehydrogenation of isopentenes (Shell), and the cracking of 2-methylpentene-2 (Scientific Design—Goodyear).

The dehydrogenation of isopentenes (see previous section) is carried out over the Dow calcium-nickel phosphate catalyst, broadly as described above for the dehydrogenation of n-butenes to butadiene. From the C_5 product, pure isoprene is recovered via acetonitrile extractive distillation to separate dienes, mainly isoprene plus piperylene (pentadiene-1,3), from olefins and saturated hydrocarbons. The diene-rich fraction recovered from the acetonitrile solution is fractionally distilled to separate polymerization grade isoprene.

The process from propylene via 2-methyl pentene-2 is described under reactions of propylene (see below).

Mixed Heptenes

In Chapter 15 the co-polymerization of propylene and n-butenes to produce a 'cat-poly' gasoline is described. A C_7 cut can be isolated from this gasoline by distillation, the conditions being chosen to yield a product containing mainly 2,3-dimethylpentene-2, 3,4-dimethylpentene-2, and 2-methylhexene-2, with a ratio (total dimethylpentenes)/(total methylhexenes) of about 2. Such a heptene fraction is a suitable feed for the production of iso-octanols via the oxo reaction.

Other higher olefins are made by wax-cracking, etc., and will be dealt with in a later section.

Benzene, Toluene, and the Xylenes (BTX)

Previous to the development of petroleum chemical sources, the main source of aromatic hydrocarbons throughout the world was coal-tar. Today benzene, toluene, and the xylenes are major petroleum chemical intermediates, and the relative importance of coal-tar has declined. These aromatics are treated together for convenience because much of their production and isolation is carried out by common or closely-related processes.

The most important route to C_6–C_8 aromatic hydrocarbons is the catalytic reforming of naphtha, a refinery operation described in Chapter 14. The original objective of reforming was to produce a gasoline of high octane number for the oil industry. With the development of methods for recovering aromatics from catalytic reformate the production of BTX from this source started to grow in the early 1950s, initially in the USA, and has been for a long time now the largest source of aromatics in that country. The same position has recently been reached in Europe, although as late as 1965 the main source of benzene was still coal-tar.

A second petroleum chemical source of aromatics is the gasoline produced by steam-cracking naphtha (see section on ethylene). In Japan this is still a more

important source than catalytic reformate. In Western Europe in 1968 aromatics capacity from steam-cracked gasoline was less than that from reformate, but more than that from coal-tar.

Other sources of benzene are the hydrodealkylation of toluene, a hydrocarbon which is often in over-supply, and the pyrolysis of steam-cracked gasoline in the presence of hydrogen.

BTX from catalytic reformate

Catalytic reformate contains mainly aromatic and paraffinic hydrocarbons, the detailed composition depending on the boiling-range and crude source of the feed to the reformer, and on the severity of reforming. The following would be typical:

A feedstock of boiling-range approximately 75–140°C is catalytically reformed to yield a reformate which is distilled to give a cut of about the same boiling-range, containing benzene 7 per cent, toluene 20 per cent, and xylenes plus ethylbenzene 16% wt. This fraction is the feed to a BTX extraction unit. In addition to BTX the reformate heart-cut contains C_9 aromatics and C_6 C_7 paraffins and naphthenes. Most of the C_8 and higher paraffins and the naphthenes are converted during reforming.

The boiling points of the aromatics in question are:

	Boiling point (°C)
Benzene	80.1
Toluene	110.6
Ethylbenzene	136.1
Para-xylene	138.3
Meta-xylene	139.1
Ortho-xylene	144.4

If only benzene, or benzene/toluene are required, then the boiling-range of the heart-cut is adjusted accordingly, and the remaining material is added to the gasoline pool. As a general case, the recovery of a mixture of benzene, toluene, and the C_8 aromatics will be described.

Processes for the recovery of BTX from catalytic reformates are of two types: (1) by liquid–liquid extraction and (2) by extractive distillation. The former was the first to be developed, but the latter is particularly useful for extracting a single aromatic from a reformate of relatively narrow boiling range.

The Udex (Dow and Universal Oil Products) process was first in the field in 1951, and is based on a diethylene- or dipropylene-glycol mixture with water. For aromatics units built since the late 1950s the Shell Sulfolane process was preferred, although many Udex plants still operate today. The Sulfolane process is based on tetrahydrothiophen-1,1-dioxide as the solvent made by reacting butadiene with sulphur dioxide followed by hydrogenation. It is usually known as 'Sulfolane'. Later still, two Lurgi processes, in which N-methylpyrrolidone (and later a mixture of NMP and ethylene glycol) is the extraction medium, made by catalytic reduction of maleic anhydride to *γ*-butyrolactone and then reaction with methylamine were introduced. The Arosolvan liquid/liquid process is applied to the recovery of mixtures of

aromatics of more than one carbon number, whilst the Distapex extractive distillation process is applied to the recovery of single-carbon-number aromatics.

Krupp-Koppers have a process based on N-formyl morpholine, while IFP have described a process based on dimethyl sulphoxide.

Factors which determine the relative economics of the various processes are:

(a) Selectivity and capacity of the solvent for aromatics.
(b) Specific gravity; the higher this is the greater is the rate of separation of the two phases during extraction, i.e. the greater the throughput.
(c) Specific heat; the lower this is, the less is the amount of heat required to bring the solvent to extraction temperatures.
(d) Boiling point; the higher this is the more readily is the rich-solvent stripped of aromatics.
(e) Thermal stability; the more stable the solvent the less is the make-up required, and the smaller are problems of removing decomposition products.
(f) Corrosivity; this governs the materials of construction of the extraction and stripping sections of the plant.

A Sulfolane extraction unit will be described as typical of such processes (Fig. 6).

The feed is a catalytic reformate containing benzene 7.4, toluene 21.6, xylenes plus ethylbenzene 15.7, C_{9+} aromatics 4.9, non-aromatics 50.4 per cent volume.

Feed is preheated to 100°C and enters the rotating-disc extraction unit at 40 psig, countercurrent to lean solvent. The aromatics plus a small amount of

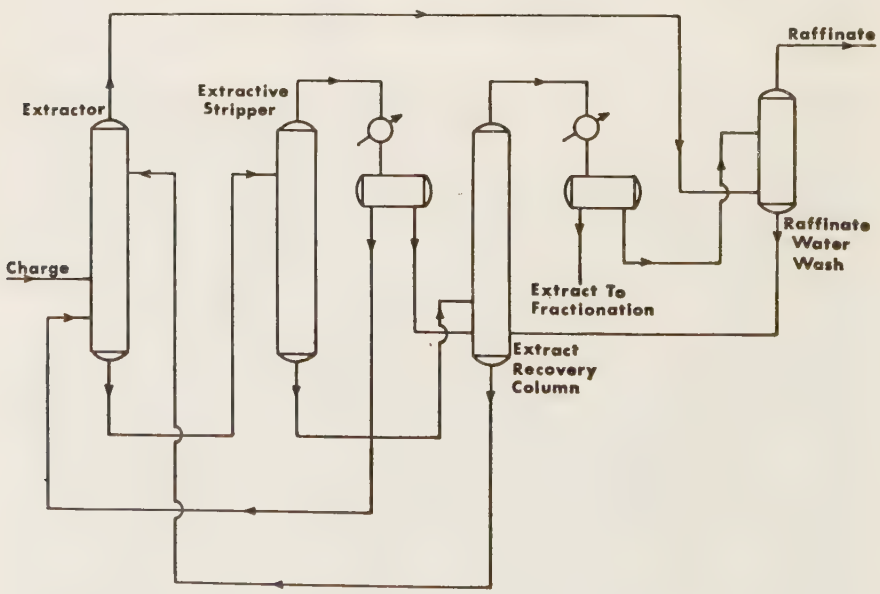


FIG. 6. Sulfolane aromatics extraction unit. (Courtesy of *European Chemical News*.)

non-aromatic hydrocarbons dissolve, and a raffinate lean in aromatics leaves the top of the extractor. This raffinate is washed with solvent-free water from the overhead of the aromatics stripper column to recover dissolved solvent, and the raffinate is then passed out of the plant. The aromatics-rich solvent leaves the base of the extractor and is passed to a column at a somewhat higher temperature and lower pressure where the non-aromatic, plus some aromatic, hydrocarbons pass overhead and are sent back to the extraction unit. The bottom product is sent to the aromatics stripper which operates at 190°C and a pressure of about 5 psia at the top. BTX passes overhead, and a small amount of water passing with it is allowed to settle and is recycled to the raffinate washer. No sulfolane passes overhead in the aromatics stream, which is then split into benzene, toluene, and the C_8 aromatics by conventional fractional distillation. Lean solvent passes out of the aromatics stripper column as bottoms, and is recycled to the extraction column.

Xylenes and ethylbenzene: C_8 aromatics separation

Whereas highly-pure benzene and toluene are easily separated from each other, and from the C_8 aromatics, by fractional distillation (see above Table of boiling points), the latter require a more complex treatment for their separation into individual isomers. The main demand is for *ortho-* and *para-*xylenes. Ethylbenzene is recovered from the C_8 stream in a few plants (the bulk is made from benzene and ethylene, as described below) and small amounts of *meta-*xylene are recovered in a few locations.

Ethylbenzene, as the lowest-boiling isomer, may be recovered by superfractionation in a state pure enough for styrene production. In most plants, however, this is not practised, and in the following typical example the recovery of only *ortho-* and *para-*xylenes from a catalytic reformate is described (Fig. 7).

A typical feed would be of composition:

Paraffins + naphthenes 34, benzene 8, toluene 18, ethylbenzene 4, *ortho-*xylene 5, *meta-*xylene 10, *para-*xylene 5, C_{9+} 16% wt.

This is fed to pre-fractionator No. 1 where a C_8–C_9 cut is taken as bottoms and passed to pre-fractionator No. 2, to remove C_{9+} hydrocarbons at the base and to obtain a C_8 fraction overhead containing typically:

Toluene 1.2, ethylbenzene 10.9, *p-*xylene 18.8, *m-*xylene 39.9, *o-*xylene 18.2, and C_9 11.0% wt.

The boiling-point difference between *ortho-*xylene and the other isomers is sufficient to permit the former to be separated by distillation in the isomer splitter which takes virtually all of the *meta-* and *para-*xylenes overhead and produces a base fraction rich in *ortho-*xylene. The latter is fed to the *ortho-*xylene column for final purification, to yield a product of specification purity for phthalic anhydride manufacture. The *meta/para* fraction cannot easily be further split by distillation and use is made of the fact that when this is cooled, pure *para-*xylene can be crystallized out. This operation is complicated by the existence of a *meta/para* eutectic of mp −53°C containing 13 per cent *para-*xylene. The *meta/para* fraction is cooled to about −65°C and crystals of *para-*xylene

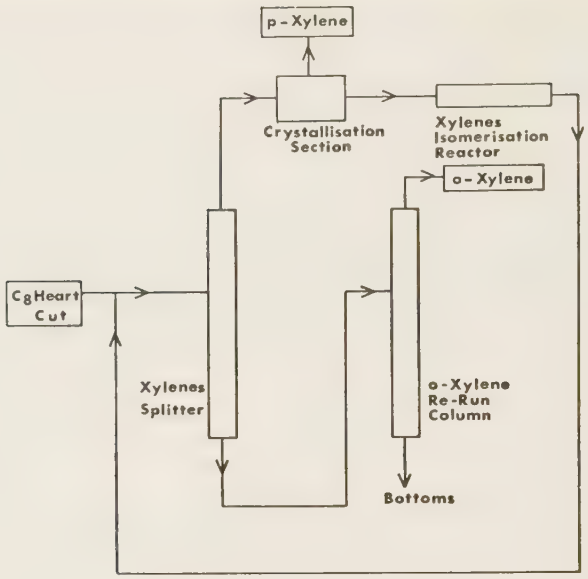


FIG. 7. Xylenes recovery process.

separate, contaminated by some eutectic. The solid is collected by centrifuging, and is transferred to vessels in which it is partially melted to give a liquid phase rich in *meta*-xylene which is again separated from the crystals, now richer in *para*-xylene, by centrifuging. The process is repeated a number of times until *para*-xylene is obtained pure enough for terephthalic acid manufacture.

The mother liquor rejected from the crystallization stage can be either sent to the gasoline pool or, more commonly, fed to an isomerization unit in which equilibrium between the xylenes is re-established by a catalytic reaction:

	% wt in	
	Typical mother liquor	Equilibrium mixture at 454°C
Ethylbenzene	18	8.5
Ortho-xylene	11	21.5
Meta-xylene	63	47.5
Para-xylene	8	22.5
	100.0	100.0

Isomerization results effectively in the conversion of *meta*-xylene into *ortho*- plus *para*-xylenes. Some ethylbenzene may enter into the isomerization depending on the type of catalyst used. There are two types:

(a) Supported platinum metal, used under hydrogen pressure (Universal Oil Products Isomar process, and Engelhard-Atlantic Octafining).

(b) Metal oxide mixtures which can operate with (Esso Isoforming process) or without (Shell process) hydrogen.

In general, some ethylbenzene isomerization to xylenes occurs on the metal catalysts, but not on oxide catalysts.

The product of isomerization is recycled to the isomer splitter for recovery of the *ortho*- and *para*-xylenes.

Reference to the boiling points of the C_8 aromatics shows that if *meta*-xylene could be removed from the mixture then the remaining isomers could be separated by conventional distillation. The Japan Gas Co. claimed the operation of a new process based upon the above scheme in October 1968. The C_8 aromatics fraction is allowed to contact a mixture of hydrogen fluoride and boron trifluoride, when a complex of *meta*-xylene only is formed in the solvent. Phase separation leads to a raffinate stream free from the *meta*-isomer, the remaining isomers being separated by distillation as outlined above. It is possible that in order to obtain *para*-xylene of the desired purity a crystallization stage may be necessary. Very pure *meta*-xylene is recoverable from the extract, but this has only limited use in down-stream products. If, however, the mother liquor containing the $HF-BF_3$ complex is heated the whole isomerizes to the equilibrium mixture.

p-Xylene can also be separated by adsorption processes, e.g. the Parex process. A simulated moving bed of adsorbent is used and at temperatures of 150–175 °C and a pressure of 10 atm the adsorbent has a greater affinity for *p*-xylene which can then be separated with a purity of 99.5 per cent.

Benzene and toluene from steam-cracked gasoline

In Western Europe and Japan, where naphtha cracking is widely practised for olefins production, large quantities of cracked gasoline containing recoverable amounts of benzene and toluene are available. The aromatics concentration in steam-cracked gasoline depends on the composition of the feed, and on the cracking severity, rising with increasing severity as the non-aromatic hydrocarbons are more completely destroyed. Thermal de-alkylation of alkyl aromatics occurs during cracking, so that benzene and toluene are the major surviving aromatics in the liquid product. At the expense of the ethylene the proportion of liquids, and hence aromatics, can be increased by raising the residence time in the furnace.

Before the BT is extracted a heart-cut is taken of bp approx. 70–120 °C, dienes are converted into olefins by hydrogenation, and then mono-olefins are reduced to saturated hydrocarbons under more severe hydrogenation conditions. This is necessary because the solvents used for the selective extraction of aromatics are also good solvents for unsaturated hydrocarbons. The product, now containing only aromatic and saturated hydrocarbons, is extracted with, e.g. 12 per cent water in N-methylpyrrolidone (Lurgi Arosolvan process), in a unit similar in principle to the BTX extraction unit described above. The BT mixture is finally separated by distillation.

The high melting point of benzene, +5.5 °C has led to processes which can extract benzene from a benzene-rich mixture by crystallization of the benzene at low temperatures. It is believed, however, that such processes are no longer used.

An alternative method of producing benzene only from steam-cracked gasoline is to thermally hydrodealkylate it in the presence of hydrogen at about

600 C, Hydrocarbon Research Inc. HDA process, Mitsubishi Petrochemical MHC process, and Houdry Pyrotol process). Non-aromatic hydrocarbons are converted into lower alkanes by a mixture of cracking and hydrogenation, and alkyl groups in aromatic rings are converted to benzene and lower alkanes (mainly methane). Pure benzene can be isolated from the liquid product by fractional distillation.

Benzene from alkyl aromatics by hydrodealkylation

The demand for benzene is much greater than that for the other aromatic hydrocarbons and the latter, particularly toluene, serve as a source of benzene by reaction with hydrogen in either purely thermal or catalytic processes, e.g. dealkylation processes can be either thermal or catalytic.

Thermal processes operate at high temperatures, e.g. 700 °C, and at pressures of, e.g. 30 atm. They have the advantage of being continuous as there are no shut-downs to clean or renew the catalyst. On the other hand the high temperatures necessary make them less thermally efficient than the catalytic processes, and there are some corrosion problems. The feedstock must be free from olefins and sulphur compounds, which in practice means a mild catalytic hydrogenation before the dealkylation process itself commences.

An important catalytic process is the Houdry-Pyrotol which both dealkylates and purifies. In theory the process will produce benzene from feedstocks containing a wide variety of hydrocarbons, but in practice C_3 and lighter are removed as well as most of the C_9s and all higher fractions, otherwise hydrogen consumption is excessive. Again it is usual to remove any unsaturated hydrocarbons to reduce coking and deposits on the main catalyst. The effluent with hydrogen is then passed into the Pyrotol catalyst beds which not only causes dealkylation of toluene and, if present, higher alkyl benzene but also converts any sulphur compounds to hydrogen sulphide and cracks any non-aromatics. The type of catalyst used may be a metal or a metal oxide on an alumina or silica support. The reaction is carried out at about 600 °C and at about 50 atm. The benzene is usually given a clay treatment to remove final traces of impurities.

Where the demand for xylenes is considerable, as well as benzene, toluene can be disproportionated to a mixture of benzene and xylenes (but very little ethyl benzene). This process is particularly useful for treating pyrolysis gasoline. The simplified reaction is:

$$2C_6H_5CH_3 = C_6H_6 + C_6H_4(CH_3)_2$$

Reformate may, however, contain substantial quantities of trimethyl benzenes in the C_9 stream. In this case a transalkylation reaction is to be preferred, the outline reaction being:

$$C_6H_5CH_3 + C_6H_3(CH_3)_3 = 2C_6H_4(CH_3)_2$$

Broadly there is little difference between disproportionation and transalkylation processes; which takes place depends upon feedstocks. Catalytic processes are, however, almost always used when transalkylation is required. The Tatoray process is suitable and is believed to use a fixed-bed catalyst

consisting of a noble metal or rare earth on alumina. Hydrogen is always present and a rather lower temperature, e.g. 400–500°C, is used in the conversion which is carried out at about 30 atm pressure.

Ethylbenzene, Styrene and its Polymers

Ethylbenzene

The only use for ethylbenzene is for the production of styrene and, more recently, of propylene oxide as a co-product (see below).

Some ethylbenzene is isolated from the C_8 fraction of catalytic reformate by direct superfractionation (see above), but by far the largest tonnage is synthesized by alkylating benzene with ethylene in the liquid phase (aluminium trichloride catalysed) or vapour phase (supported phosphoric acid catalyst):

$$C_6H_6 + C_2H_4 \longrightarrow C_6H_5C_2H_5$$

In the liquid-phase process benzene is carefully dried by azeotropic distillation, and is fed with ethylene to a glass-lined, stirred vessel in which aluminium chloride plus a little ethyl chloride are present in the form of a dense liquid phase containing a complex of $AlCl_3$ with benzene and mono/poly ethylbenzenes. The function of the ethyl chloride is to generate hydrogen chloride essential for the formation of the active catalyst. The alkylation temperature is 140–200°C, the pressure 4–9 atm and the reaction time 30 min, under which conditions mono- and some polyethylbenzenes are formed to give an effluent of approximate composition: benzene 47, ethylbenzene 39, polyethylbenzenes and other high-boiling materials 14 per cent. The effluent passes to a settler where the lower layer of catalyst complex is removed and recycled to the reactor, whilst the upper layer is removed, washed with water and caustic soda to remove inorganic matter, and finally fractionally distilled in three columns to separate benzene (recycled), ethylbenzene, polyethylbenzenes (recycled), and a heavy residue which is rejected. Recycle of the polyethylbenzenes to the alkylation reactor prevents their build-up in the system, since the alkylation reaction is reversible in the presence of the catalyst.

The vapour-phase process for ethylbenzene production is a conventional fixed-bed catalytic process in which a mixture of ethylene and excess benzene is passed over a supported phosphoric acid (or possibly silica-alumina) catalyst at about 300°C and 40 atm. The products are worked up by fractional distillation in the usual way. This process is, however, very little used today.

Styrene

The dehydrogenation of ethylbenzene:

$$C_6H_5C_2H_5 \longrightarrow C_6H_5CH{=}CH_2 + H_2$$

is strongly endothermic and is carried out at 600°–650°C and at low hydrocarbon partial pressure achieved by steam dilution (15 mol/mol hydrocarbon). Mixed oxide catalysts are used, two common ones being the Standard Oil 1707 type (Fe_2O_3 18.4, K_2O 4.6, CuO 4.6, and MgO 72.4% wt) and the Shell catalyst (Cr_2O_3 and K_2O on Fe_2O_3).

The steam is heated to 710°C and is mixed with ethylbenzene heated to only 500°C to avoid decomposition prior to the reactor. The mixture enters the reactor at 600°–620°C for fresh catalyst, higher temperatures (max 650°C) being used as the catalyst ages. Dehydrogenation accompanied by some coke lay-down occurs, and a further function of the steam is to remove coke via the water–gas reaction, thus affording a catalyst life of about one year, the catalyst being non-regenerable. Ethylbenzene conversion is about 40 per cent per pass. Gaseous products are vented and a liquid product is obtained consisting of styrene, ethylbenzene, small amounts of benzene and toluene, and tar. These are contacted with elemental sulphur, which acts as an inhibitor for styrene polymerization, before being passed to a series of fractional distillation columns for the recovery of polymerization grade styrene (99.9 per cent pure). Tertiary-butyl catechol is added to the final product as a polymerization inhibitor.

Modern processes are extremely efficient. Ethylbenzene is obtained in 96 and 97 per cent yield on benzene and ethylene respectively, and styrene in 90–92 per cent yield on ethylbenzene.

Instead of dehydrogenating the ethyl benzene the latter can be peroxidized by air oxidation in the presence of an oxidation initiator. At about 90°C and 100 atm pressure ethyl benzene peroxide reacts with propylene over a molybdenum naphthenate catalyst to form propylene oxide and phenylmethyl carbinol, which itself can be dehydrated to styrene over a titanium dioxide catalyst in the vapour phase at 180°C. The cost of the styrene produced by this process depends on the value that can be placed on the co-product, propylene oxide, which itself depends on the demand for propylene oxide and its cost by conventional processes (see below). Several plants are, however, in operation using this route to styrene.

Uses of Styrene

Polystyrene

A long established thermoplastic produced by polymerizing styrene, usually either by the influence of heat in bulk or by suspension techniques in the presence of a catalyst such as benzoyl peroxide. Polystyrene made by these methods is a transparent, brittle material, which, because of its wide temperature range in softening, is the ideal material for injection moulding. It is used on a major scale for making fancy articles, and also for electric light fittings.

At the expense of transparency a less brittle material, 'high-impact polystyrene' can be made, e.g. by dissolving about 10 per cent of polybutadiene rubber in the styrene before polymerization.

Foamed polystyrene is another important modification and can be made by incorporating a low-boiling liquid such as pentane in the styrene and then suspension-polymerizing it. The product has found many uses in insulation and lightweight packaging.

Styrene co-polymers

By far the largest consumer is the production of the major general-purpose synthetic rubber in the production of which it is co-polymerized with about

three times its weight of butadiene. Another major use is in the production of ABS in which styrene, butadiene, and acrylonitrile are co-polymerized by various techniques and yield a tough moulding powder. Styrene acrylonitrile co-polymer is also made on a smaller scale and has a slightly higher heat distortion point than straight polystyrene.

Other uses

Styrene is used in some types of surface coatings as a constituent of styrenated alkyd resins. It is also the usual cross-linking material in unsaturated polyester resins, while it is one of the base materials in the production of ion-exchange resins.

Ethyl toluene and vinyl toluene

Ethyl toluenes can be produced from ethylene and toluene by a process similar to that for making ethylbenzene. A mixture of the three isomers is produced, but the ortho must be separated by distillation as it undergoes ring formation on dehydrogenation. A mixture of *m*- and *p*-vinyl toluenes is thus produced. This mixture proved disappointing as a monomer, but has been of some value in unsaturated polyester and alkyd resins. Mobil have recently announced that by using a special zeolite catalyst only *p*-ethyl toluene is produced and this dehydrogenates to *p*-vinyl toluene (which Mobil call PMS). The polymer thus produced shows marginal improvements over polystyrene and has better flow characteristics.

Cumene

Cumene (isopropylbenzene) is manufactured from benzene and propylene by alkylation, via routes which are similar to those used (see above) for ethylbenzene production, i.e. a liquid-phase process with an aluminium chloride catalyst, or a vapour-phase process over phosphoric acid on kieselguhr catalyst:

$$C_6H_6 + C_3H_6 \longrightarrow C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

The product is used exclusively for conversion into phenol and acetone—see below.

Cyclohexane

Cyclohexane can be isolated from straight-run petroleum fractions by fractional distillation, but the product is not pure enough for most chemical uses, although about 250 000 tons/year is reported to be so produced in the USA. Product pure enough to serve as chemicals feedstock is normally manufactured by hydrogenating high-purity benzene, in either the vapour or the liquid phase.

At the pressures of 20–45 atm normally used in commercial operations, the equilibrium:

$$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$$

lies completely on the side of cyclohexane at below 300°C. Nickel catalysts are used in all processes excepting the Sinclair Research and the UOP Hydrar processes which are based on supported platinum. Benzene of purity above 99.5 (generally 99.8–99.9 per cent) is used since the cyclohexane purity depends closely upon that of the feed. Because nickel is poisoned by sulphur, the sulphur-content of the benzene feed must be less than 3 ppm, a specification which is met by benzene produced from catalytic reformate and from steam-cracked gasoline. Other catalyst poisons such as hydrogen sulphide, carbon monoxide, and carbon dioxide, have to be removed from the feed hydrogen for similar reasons.

There are so many processes for cyclohexane production that no single one will be described. Instead, the general features of such operations will be outlined.

Most processes involve fixed-bed, vapour-phase operations carried out at around 220°C and 20 atm, the temperature and pressure varying somewhat according to the individual process. Benzene is vaporized and mixed with a considerable excess of hydrogen (4–11 mol per mol of benzene, according to the process) before passing to the main catalytic reactor, where in single-stage processes the hydrogenation is completed. There exist two-stage processes in which about 95 per cent of the benzene is hydrogenated in the main reactor and the remainder is converted in a smaller second-stage reactor. The reduction is highly exothermic, and measures taken to dissipate the heat of reaction include: recycle of product, interstage cooling with multiple catalyst beds arranged in series, and internal or external cooling to raise steam. The final reactor effluent is sent to a gas/liquid separator whence the hydrogen is in part recycled or purged, and the liquid stream is rerun to remove dissolved gases and to yield pure cyclohexane.

In a typical liquid-phase process hydrogen is passed into a suspension of Raney nickel in benzene at 200°C/40 atm, the catalyst being maintained in suspension by vigorous circulation of the reactor contents through an external heat-exchanger where steam is raised. The contents are allowed to vaporize and the effluent is passed to a second-stage finishing reactor containing a nickel on carbon catalyst, run in the vapour phase at 160°–220°C under pressure. The final effluent is worked up as before. Alternative procedures include two-stage processes in which both stages are run in the liquid phase, and a multi-reactor liquid-phase process with interstage cooling.

The above processes yield cyclohexane of purity 99.5–99.9% wt.

Normal Paraffins

The normal paraffins are, apart from cyclohexane, the only liquid chemical intermediates which can be isolated from straight-run fractions of crude oil by simple physical processes, and yet their appearance on the petroleum chemical scene is quite recent (late 1950s). There are two types of process in use commercially:

(a) For n-paraffins in the kerosine range, C_{10}–C_{13}, and the gas oil range, C_{14}–C_{18}, selective absorption into synthetic zeolites (molecular sieves) is used.

(b) For n-paraffins in the paraffin wax range of about C_{25}–C_{30}, urea adduction is practised.

Both are physico-chemical processes and rely upon the difference in cross-sectional area between the n-paraffins (diameter of cross-section about 4.9 Å) and the isoparaffins, naphthenes, and aromatics (all greater than 5.6 Å). In sieve processes the absorbent is a crystalline alumino-silicate which in the sodium/calcium form consists of large internal cavities, access to which is via ports of diameter 5 Å. Thus only n-paraffins in a straight-run oil fraction can enter the internal voids of the sieve, the remaining hydrocarbons not being absorbed.

The basis of urea adduction is somewhat different. In the presence of n-paraffins, urea will crystallize in a form which accommodates n-paraffin molecules within the crystal structure, the crystal geometry being such that molecules of other hydrocarbon types are not accommodated.

Molecular sieve processes

The extraction of n-paraffins from kerosine or gas oil is carried out on a conventionally-desulphurized feedstock. Extraction can occur from the liquid phase (Molex process of UOP) or vapour phase (BP, Linde IsoSiv, or Texaco processes). Desorption of the n-paraffins can be achieved by displacement with a lower n-paraffin (BP, Molex and Texaco process) or by lowering the pressure (Linde IsoSiv process). The BP process will be described in more detail.

Kerosine or gas oil is vaporized and fed to a bed of 5 Å molecular sieve at a temperature sufficiently high to maintain all hydrocarbons in the vapour phase and to ensure an adequate rate of absorption of n-paraffins, but not high enough to cause cracking of the feed. The pressure is maintained constant and positive. At the end of the absorption cycle the flow of feed is replaced by an inert gas (nitrogen or hydrogen, for example) and a short purge cycle is operated to remove non-normal hydrocarbons adsorbed on the sieve surface or otherwise held up in the void spaces of the absorber. The absorber now contains only sieve loaded with n-paraffins, and a lower n-paraffin (e.g. n-pentane) is admitted to cause displacement of the kerosine or gas oil n-paraffins. The amount of desired n-paraffin displaced falls off with time, and the duration of the displacement cycle has to be optimized to balance the recovery of extra product per cycle against the time spent in doing so. At the end of the desorption cycle the sieve contains the displacing n-paraffin plus residual gas oil or kerosine n-paraffins, and is ready for the next absorption cycle. By linking four absorbers in parallel the overall process is made continuous, with one absorber on absorption, one on purge, one on desorption, and one on standby or regeneration. The n-paraffin and raffinate streams are sent to conventional distillation columns for the removal of the displacing paraffin and the recovery of pure n-paraffin product.

A small amount of coke deposition occurs on the sieves, and they are occasionally regenerated by a conventional burning-off procedure. The overall life of the molecular sieves is reckoned to be at least four years.

After appropriate finishing treatments which depend on the end-uses of the products, (a) the kerosine n-paraffins are available for, e.g. detergent (linear alkyl benzene sulphonate) production, and (b) the gas oil n-paraffins for, e.g. polychlorination to yield a secondary plasticizer for PVC, or monochlorination followed by dehydrochlorination to yield n-olefins also used in detergents production. The n-paraffin content is commonly 98 per cent or more.

Urea adduction

For the extraction of n-paraffins of carbon number above 18 the rates of adsorption and desorption on molecular sieves are too slow for the above type of process to be attractive, and for these hydrocarbons urea adduction is used. The only important application for petrochemical use is the recovery of C_{25}–C_{30} n-paraffins from vacuum distillates, the product being required for steam-cracking to alpha-olefins (see below).

In the Edeleanu process the feedstock is mixed with methylene chloride and stirred with a saturated aqueous solution of urea at 40°C. The n-paraffin-urea adduct separates as crystals (granulation is improved by the methylene chloride) which are removed by filtration and washed with methylene chloride. The adduct is passed to a vessel in which it is decomposed at 80°C by heating with water, to yield a paraffin phase and an aqueous urea phase, subsequently separated in a settler. The urea phase is reconcentrated before recycle, and the n-paraffin phase is topped to remove small amounts of solvent, yielding a final product containing about 95 and 5 per cent of normal and branched paraffins respectively.

Linear Olefins

Linear olefins in the C_6–C_{18} range find a variety of uses depending on the carbon number and the position of the double bond. Alpha-olefins are manufactured by:

(a) Wax-cracking, i.e. steam-cracking of C_{25}–C_{30} n-paraffins from the urea-adduction process.
(b) Oligomerization of ethylene via an aluminium alkyl catalyst.

Internal linear olefins are prepared by the chlorination/dehydrochlorination of C_{11}–C_{13} n-paraffins from molecular sieve extraction processes.

The production of linear olefins by oligomerization of ethylene will be described under ethylene derivatives.

DERIVATIVES OF THE PARAFFINS

Hydrogen and Carbon Monoxide

One of the oldest of the reactions of the paraffins, usually called reforming, consists, virtually, in breaking them down into their constituent elements, which are more useful units for the building of other molecules. The actual product of the reaction is a mixture of carbon monoxide and hydrogen, called synthesis gas, which formerly was made by the action of steam on coal (water–

gas reaction), $C + H_2O \rightarrow CO + H_2$, but methane and the paraffins generally are now much more important feedstocks.

The first reforming process consists in the reaction of steam with methane or naphtha:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = 50\,\text{kcal}$$

This endothermic reaction is subject to an equilibrium that moves in favour of CO and H_2 with increasing temperature and with decreasing pressure. It is usually conducted at a relatively high pressure, about 30 atm, in order to take advantage of the pressure at which the feedstocks are available and supply the products at the high pressure required for synthesis purposes. A supported nickel oxide catalyst, contained in gas-flame heated tubular reactors, is used, and to prevent poisoning of this the feedstock must be desulphurized. To some extent the adverse effect of pressure on the equilibrium is compensated by high reaction temperature, 900–1000°C, and the use of excess steam; nevertheless, some hydrocarbon remains unconverted, and to remove this it is necessary to add a little air to the gas and pass it into a second reactor where oxidation of hydrocarbon takes place.

In the alternative reforming process a mixture of hydrocarbons (which can be anything from methane to heavy fuel oil), oxygen, and steam is fed to a large tubular reactor containing no catalyst at about 1300°C and 40 atm pressure. A complicated series of reactions ensues, but the net result is that at this high temperature the endothermic reaction with steam takes place, without catalyst, together with the exothermic partial oxidation:

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2 \qquad \Delta H = -8.5\,\text{kcal}$$

Temperature control is therefore possible by proportioning the feed so that one reaction suitably offsets the other.

An adjunct to the reforming process, useful in adjusting the CO/H_2 ratio for particular syntheses, is the reaction:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

Carbon monoxide may be isolated from synthesis gas by liquefaction or selective absorption in cuprous ammonium salt solutions. In order to isolate hydrogen the synthesis gas is first subjected to the shift reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -10\,\text{kcal}$$

which eliminates most of the CO. The shift reaction is applied in two catalyst charged reactors in series, the first operating at high temperature so that most of the conversion occurs there quickly, the second operating at much lower temperature, about 240°C, so that the final equilibrium composition is more favourable. CO_2 is then washed out of the gas by ethanolamine or potassium carbonate solution. Remaining traces of carbon oxides may be removed by passing the gas over a nickel catalyst at moderate temperature and at a pressure of 20 atm. In this reactor the reverse of the methane reforming reaction occurs, i.e. CO and H_2 are converted back to methane and water, because of the large excess of hydrogen, under pressure, at fairly low temperature.

Hydrogen is used above all for the manufacture of ammonia by its reaction with nitrogen, and is also consumed in various refining and petrochemical operations such as hydrocracking, hydrorefining, hydrogenation of nitriles to amines and of phenol to cyclohexanol. Some of the applications of CO alone or of the mixture of CO and H_2 will be described subsequently.

Production of Methanol from Hydrogen and Carbon Monoxide

For methanol production pure hydrogen is not required so the shift reaction is not needed. Both carbon monoxide and carbon dioxide will react with hydrogen under the appropriate conditions to give methanol, the basic reactions being:

$$CO + 2H_2 = CH_3OH$$

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

In the traditional process the mixed gas stream, adjusted to a suitable composition, is compressed to some 300 atm and heated to 300–400°C. It is then passed into a converter where in the presence of zinc oxide promoted with chromium oxide the reaction takes place. It is an exothermic reaction and cooling is necessary. However, in recent years ICI have developed a low-pressure process where the converter pressure is 100 atm and the temperature 250°C. Rather than add carbon dioxide to bring the ratio to hydrogen correct for methanol surplus hydrogen is frequently purged and its energy content recovered. Copper-based catalysts are normally used but they are easily poisoned, e.g. by sulphur compounds, and the feedstock must be freed from the latter.

Methanol is now made on an enormous scale world-wide, and nearly half is converted to formaldehyde. About half the formaldehyde is used to produce urea, melamine, and phenolic resins.

Methanol can be reacted with carbon monoxide in the presence of a rhodium catalyst promoted with iodine to give acetic acid. The carbon monoxide need not be free from hydrogen, and this reaction shows such promise that it may displace an earlier route for the production of acetic acid by the oxidation of paraffins.

A new process is being developed and a plant under construction for the production of acetic anhydride from methanol which will greatly assist the viability of the production of cellulose acetate. Dimethyl ether is produced from methyl alcohol by conventional means and this, when reacted with carbon monoxide in the presence of rhodium, again using iodine as a promoter, forms first methyl acetate and then acetic anhydride.

Mobil have developed a process and a plant is being built in New Zealand by which methanol can be converted to gasoline. A zeolite catalyst is used, a pressure of 5 atm and a temperature of 350°C. An excellent yield (90 per cent) of a high-grade gasoline containing mainly branched-chain paraffins together with aromatics is produced.

Production of formaldehyde from methanol

The old established method of converting methanol to formaldehyde involves passing a gaseous mixture of about 30 per cent methanol in air at 400–500°C

over a silver catalyst. Because the proportion of air is restricted the endothermic dehydrogenation, $CH_3OH \rightarrow CH_2O + H_2$, takes place as well as the exothermic oxidation, $CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$, and the consequent limitation of heat output enables the whole reaction to be carried out in a nearly adiabatic manner. Unreacted methanol serves as a stabilizer in the product 'formalin', an aqueous solution containing 30–40 per cent CH_2O.

In a process more recently introduced, methanol is converted into formaldehyde entirely by oxidation, by reaction with an excess of air over an iron oxide/molybdenum oxide catalyst. This process, operating at a lower temperature, competes with but does not entirely replace the older process.

Production of ethylene glycol from hydrogen and carbon monoxide

This can be obtained from carbon monoxide and hydrogen using a rhodium catalyst, a temperature of 500°C, and at approx. 750 atm. It is, however, doubtful whether this will ever be able to compete with existing processes (see under derivatives of ethylene).

Production of olefins from hydrogen and carbon monoxide

A mixture of carbon monoxide and hydrogen at 21 atm and 280°C, passed through medium-pore silicalite containing iron or manganese compounds as catalyst with a potassium compound as promoter, yields 40 per cent of C_2–C_4 olefins. Zeolite 2SM5 has also been used, but the yield is lower and the product largely aromatic. Another catalyst is Zeolite AM 450 and this yields 16–30 per cent of ethylene and 29–37 per cent propylene.

Hydrogen cyanide, production from methane

Hydrogen cyanide was an important derivative of methane which, reacted with ammonia at temperatures of over 1000°C, produced this product. Hydrogen cyanide used to be reacted with acetylene to give acrylonitrile, but the modern method of making acrylonitrile from propylene results in considerable quantities of hydrogen cyanide as a by-product, and generally this is sufficient (see below).

The most important use for this chemical is its reaction with acetone to give acetone cyanhydrin which with methyl alcohol and sulphuric acid gives methyl methacrylate. This readily polymerizes to polymethymethacrylate, a hard transparent polymer largely produced as sheet. Other uses are in dentures, while the monomer is sometimes used as a cross-linking agent (instead of styrene) in unsaturated polyester resins.

Oxidation of Paraffins—Acetic Acid

Whereas the oxidation (by molecular oxygen) of an olefin is amenable to specific catalysis, resulting in selective conversion into a product that retains the original carbon chain structure, unbranched paraffin molecules, in general, offer no preferred site for attack, which therefore occurs at random along the chain, is little influenced by catalysts, and results in extensive rupture of

carbon–carbon bonds. Paraffin oxidation proceeds by a free-radical mechanism, initiated by alkyl peroxy radicals, and leads to a mixture of oxygenated compounds rendered the more complex by the fact that the initial products of oxidation may undergo further reaction either with oxygen or with each other. Fortunately, acetic acid, the most important of the aliphatic acids, is also one of the most stable and most resistant to further oxidative attack of all the possible products, and by proper control of reaction variables it is possible to direct the reaction largely towards acetic acid.

It is believed that the Celanese Corporation of America operates the vapour phase oxidation of butane (at about 350°C, 8 atm) to obtain a mixture containing most of the lower (up to C_4) aldehydes, acids, alcohols, esters, and ketones, in which acetaldehyde and acetic acid predominate. A very complex distillation train is needed for the separation of these products.

Greater selectivity with respect to acetic acid is achieved in liquid-phase oxidation where the reaction is more intense. For this purpose, Celanese, Huls, and others use butane as feedstock, while BP use a petroleum cut consisting mainly of C_5–C_7 paraffins. In the BP process air and hydrocarbons are fed to a tower reactor operating at about 160°C under a pressure of 50 atm. The liquid in which the reaction occurs consists mainly of oxidation products which are continuously produced and continuously removed, partly as liquid and partly as vapour. The air is fed at the bottom of the reactor to assist with good contacting of the liquid and vapour phases, which together with close control of temperature is essential for complete reaction of oxygen and high yield of acid. Gaseous product from the top of the reactor is cooled first to ambient temperature and then below 0°C to condense volatile reaction products and unconverted hydrocarbons, which are recycled. Liquid product from the bottom of the reactor is transferred to the distillation system, where more volatile products are first distilled out, which are also returned to the reactor. Water, formed in the reaction, is then eliminated by azeotropic distillation with an entraining agent, leaving a mixture of formic, acetic, and propionic acids, which are separated by further fractional distillations. Acetic acid constitutes the major part of the product, but all three acids are produced in a very pure condition.

Acetic acid, easily the most important of all the aliphatic acids, is consumed mainly in the manufacture of cellulose acetate, vinyl acetate and other esters. The paraffin oxidation route has the advantage of using cheap feedstocks and reagents, but requires high capital investment in compressors and corrosion-resistant pressure reactors.

As mentioned in the previous section new plants for the production of acetic acid may use the direct route from methanol.

Chlorine Derivatives

Methane forms four chloro derivatives, all can be made by the direct chlorination of methane, but methyl chloride CH_3Cl is usually made by the reaction of methanol with hydrochloric acid at 350°C over calcined alumina or zinc chloride on pumice. Higher chlorine derivatives are normally made by the further chlorination of methyl chloride, a reaction which can be stimulated by u.v. light. The hydrogen chloride released can be used to make more methyl

chloride, though a process is coming on stream in Japan which oxidizes the hydrogen chloride back to chlorine using a catalyst of cuprous- cupric-potassium chlorides.

Methyl chloride is mainly used in the production of silicones and tetramethyl lead. Methylene dichloride, CH_2Cl_2, has a major use as a paint-remover and degreasing agent. Chloroform, $CHCl_3$, was important as an anaesthetic but has now been almost entirely superseded. Its main use now is in the production of fluorocarbons. Carbon tetrachloride, CCl_4, was used in fire extinguishers, dry cleaning, and degreasing, but most of these markets have been lost now and its main use is in the production of fluorocarbon propellants. An alternative route to carbon tetrachloride is by the reaction of chlorine on carbon disulphide. The latter is another methane derivative, now normally produced by reacting methane and sulphur vapour at 675 °C and at 2 atm pressure in the presence of activated alumina or a special clay. Besides its use in the production of carbon tetrachloride it is used on a considerable scale in the production of viscose rayon.

Several chlorine derivatives of ethane and ethylene, in particular trichloroethylene, $CHCl{=}CCl_2$, and tetrachloroethylene, $CCl_2{=}CCl_2$, are used for dry cleaning and for metal degreasing.

Ethyl chloride, an intermediate in the production of the anti-knock compound, tetraethyl lead, is made by the reaction of hydrogen chloride with ethylene or ethanol, and by the monochlorination of ethane. A disadvantage of the substitutive chlorination of hydrocarbons is the production of hydrogen chloride by-product, $RH + Cl_2 \rightarrow RCl + HCl$. This disadvantage is eliminated in the Shell process for ethyl chloride which utilizes two reactors in series. In the first of these ethane and chlorine react, in the gas phase, to give ethyl chloride and hydrogen chloride. Ethylene is added to the effluent gas, which then passes to a second reactor where hydrogen chloride and ethylene combine, to give more ethyl chloride, $CH_2{=}CH_2 + HCl \rightarrow CH_3{-}CH_2Cl$.

The demand for tetraethyl (and tetramethyl) lead is now falling due to many governments restricting or banning its use due to the possibility of lead poisoning.

DERIVATIVES OF ACETYLENE

Numerous important industrial products have been produced from acetylene in the past but, with the exception of butane diol described below, none of the products appears to have any long-term future when based on acetylene. Vinyl chloride and vinyl acetate can be made by the reaction of acetylene with hydrochloric and acetic acids, respectively. Vinyl chloride is, however, normally made from ethylene (see below), while the production of vinyl acetate is gradually being changed over.

Acrylonitrile (vinyl cyanide), once made from acetylene and hydrogen cyanide, is now made from propylene (see below).

Acetaldehyde is now made from ethylene, while the use of acetylene via the Reppe process for the production of acrylic acid and acrylates, is now being displaced by the use of propylene (see below).

The production of trichlorethylene and perchlorethylene has been one of the traditional areas of acetylene chemistry. Acetylene was chlorinated to give

tetrachlorethane, $CHCl_2CHCl_2$ which was then dehydrochlorinated to give trichlorethylene, $CCl_2{=}CHCl$, which itself can be chlorinated and dehydrochlorinated to give perchlorethylene, $CCl_2{=}CCl_2$. These have been used for dry-cleaning, degreasing, and also as a solvent, but doubts as to their toxic properties have caused demand to fall. They can now be made from propylene.

The one growth area for industrial acetylene chemistry seems likely to be the production of 1,4-butane diol. It is produced by the reaction of acetylene with formaldehyde under pressure to yield 1,4-butyne diol, $CH_2(OH)C{\equiv}CCH_2(OH)$. This can be hydrogenated to 1,4-butane diol. Butane diol can, by ester interchange with dimethyl terephthalate, give butene terephthalate (or tetramethylene terephthalate), which can be polymerized to polybutene terephthalate.

While the latter has some use as a fibre its main use has been in plastics, particularly in moulding, where temperature control is much easier than with polyethylene terephthalate and even relatively low molecular weight polymers are quite tough.

Other uses for 1,4-butane diol are the production of tetrahydrofurane, which is a valuable solvent, by dehydration, dehydrogenation yields butyrolactone, while reaction with ammonia gives pyrrolidines.

DERIVATIVES OF ETHYLENE

Ethylene is the feedstock used in largest amounts. It is relatively cheap and is chemically very reactive, entering into many specific reactions with the aid of catalysts. The earlier processes involving ethylene were based on the more obvious reactions of addition and oxidation. More recently, routes to vinyl compounds from ethylene have been developed, and important advances have been made in the conversion of ethylene into high polymers.

Polyethylene

This thermoplastic, now produced on an enormous scale world-wide, can be made either by high- or low-pressure processes. In the original high-pressure process, discovered by ICI in the 1930s, ethylene is polymerized with about 0.5 per cent oxygen, and 1 per cent propane to act as a chain stopper, at 200°C and 2000 atm pressure. New techniques had to be developed to compress the gas adequately and to make vessels strong enough to withstand the very high pressure. The time of contact need only be a few seconds. Various modifications have been developed by other companies, but these mostly relate to the separation of the polyethylene. In general, after separation from the unreacted ethylene, which is purified and recycled, the hot molten polyethylene, usually in the form of a thick ribbon, is forced through an extruder from which it emerges in the form of thick filaments which can be chopped to form pellets. The low-pressure process is carried out either in the presence of titanium tetrachloride-aluminium triethyl or chromium oxide on a silica alumina support. In the former method, the Ziegler process, the reaction is carried out at about 5 atm and 70°C with the catalyst suspended in an inert solvent. In the latter, the Phillips process, higher pressures are required, e.g. at about 15 atm

and a slightly higher temperature. Cyclohexane is present as a solvent, though the catalyst is again in suspension.

Polyethylene made by the high- and low-pressure processes differs in density, the former having the lower density, about 0.92, and is usually known as low-density polyethylene (LDPE), while the latter has the higher density (0.96) and is hence known as high-density polyethylene (HDPE). LDPE has a higher impact strength, while HDPE has better temperature resistance and a higher tensile strength. A major use of LDPE is in the production of film, while HDPE, which feels much stiffer, is mainly used in injection and blow-moulding, particularly to form bottles and other containers. There are many smaller applications such as extrusion coating wire, cable, and pipes.

LDPE is basically a branched-chain polymer, while HDPE is linear or nearly so. A modified polymer has recently been developed which has a density of about 0.92, but is linear and is referred to as LLDPE. It can be produced either by modified high- or low-pressure techniques. Its great advantage appears to be in film where this product will give very thin films but with a strength equal to much thicker conventional LDPE. A very bright future is predicted for this modification, one of the consequences being a reduced demand for ethylene.

Ethanol

Formerly a product of the fermentation of carbohydrates exclusively, ethanol is now largely made by the hydration of ethylene, one of the oldest petrochemical processes, and still an important one, the expansion of which has, however, been restricted by the fact that there is now little demand for ethanol for the production of acetaldehyde and acetic acid.

There are two principal methods of hydrating ethylene. The first consists in absorption of the ethylene in 95 per cent sulphuric acid, followed by the hydrolysis of the alkyl hydrogen sulphate so produced:

$$CH_2{=}CH_2 + H_2SO_4 = CH_3CH_2 \cdot O \cdot SO_2(OH)$$

$$CH_3CH_2 \cdot O \cdot SO_2(OH) + H_2O = CH_3CH_2OH + H_2SO_4$$

Disadvantages of this method are that it is in two stages, that it utilizes a corrosive reagent, and that recovery of sulphuric acid contaminated with by-products is difficult.

An alternative is the vapour-phase reaction of ethylene and water in the presence of a catalyst such as supported phosphoric acid:

$$CH_2{=}CH_2 + H_2O \rightleftharpoons C_2H_5OH \qquad \Delta H = -11 \text{ kcal.}$$

An elevated temperature (about 300°C) is required for a practical reaction rate, but the thermodynamic equilibrium becomes less favourable to alcohol formation as the temperature rises (exothermic reaction). High pressure in the reactor helps to overcome the equilibrium limitation; nevertheless, conversion is restricted to only a few per cent per pass and a large portion of the gas leaving the reactor is recycled. Alcohol is recovered in the vapour-phase process by scrubbing the reactor exit gas with water. Purification is by a series of

distillations, but may include hydrogenation in the presence of a catalyst to destroy aldehyde by-products.

Ethanol is made by both methods, but in the UK the direct vapour-phase route is preferred.

Acetaldehyde from Ethanol

Acetaldehyde is made from ethanol by vapour-phase dehydrogenation

$$C_2H_5OH \rightleftharpoons CH_3CHO + H_2 \qquad \Delta H = 15\,\text{kcal}.$$

This is an endothermic reaction (as are most dehydrogenation processes), requiring, therefore, a high temperature for favourable equilibrium conditions. Multitubular reactors charged with a copper catalyst are used, the reaction temperature being about 300°C.

Acetaldehyde is also made by the reaction of ethanol with a restricted amount of air over a silver catalyst in adiabatic reactors. These processes are, however, little used now.

Acetaldehyde by Ethylene Oxidation

In the latest method of production of acetaldehyde, known as the Wacker process, ethylene is converted directly to acetaldehyde by reaction with oxygen in a single reactor. The simple overall result of this process

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO,$$

is the sum of a complicated series of reactions, which are not fully understood. It depends, essentially, on a palladium chloride catalyst, able to form a complex or intermediate compound with ethylene, which reacts with water to yield acetaldehyde and palladium metal. Complex formation and decomposition together amount to:

$$CH_2 = CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl.$$

This result, however, is of no practical value unless the palladium can be readily converted back to the chloride, and the reaction with molecular oxygen, which may be written $Pd + \frac{1}{2}O_2 + 2HCl \rightarrow PdCl_2 + H_2O$, is actually far too slow for this purpose. The problem of re-oxidation was overcome by the use of a co-catalyst, copper chloride, which is able both to oxidize palladium metal and to be itself re-oxidized at a sufficiently fast rate:

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + (CuCl)_2$$
$$(CuCl)_2 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

There are two variants of the Wacker process. In the first of these (Fig. 8), which uses only one reactor, a feed of ethylene and oxygen (including recycle gas) is passed through a tower reactor containing a solution of palladium and copper chlorides in water. The exit gas is scrubbed with water for the removal of acetaldehyde and recycled, but a purge is taken in order to limit the

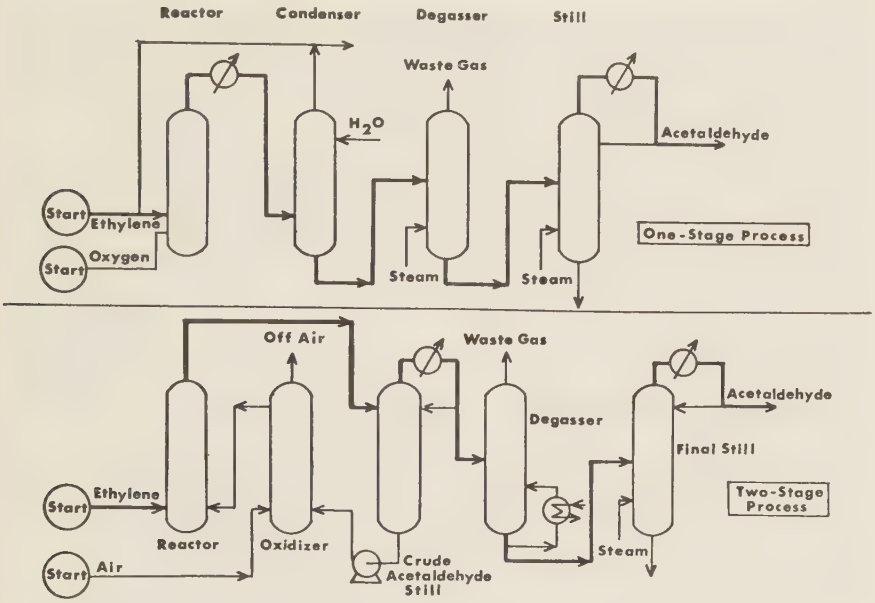


FIG. 8. Acetaldehyde from ethylene—Wacker process. (Courtesy of *Hydrocarbon Processing*.)

concentration of inert gas in the system, its size depending on the purity of the oxygen and the ethylene introduced.

In the two-stage version of the process ethylene alone is brought into contact with the catalyst solution under slight pressure. The amount of acetaldehyde formed depends strictly on the amount of cupric chloride actually present. Acetaldehyde is then distilled off by release of the pressure, and the used catalyst is pumped to a second reactor in which it is treated with air so that the metals are returned to the higher state of oxidation.

Titanium, used in the construction of the pumps and reactors, has been found sufficiently resistant to corrosion by the catalyst solution.

Vinyl Acetate

Vinyl acetate has been made in one stage from ethylene by a process which is analogous to the Wacker process, and which utilizes the same principal catalyst ingredient, palladium. But instead of water, acetic acid containing alkali metal acetate is the reaction medium. The main reaction may be pictured thus:

$$CH_2{=}CH_2 + PdCl_2 + CH_3COOH \longrightarrow CH_2{=}CHOOCCH_3 + Pd + 2HCl$$

While some plants have been built using this process, it is unlikely to make further progress.

Emphasis is now on a vapour-phase process developed by Bayer. Ethylene, oxygen, and acetic acid are reacted over a palladium on silica fixed catalyst at 175–200°C and 5–10 atm.

The modern process for producing vinyl acetate is to react ethylene, oxygen, and acetic acid with a little sodium acetate at 175–200°C and 5–10 atm over a palladium catalyst on a silica or alumina support. Reaction products are cooled to 40°C, and any vinyl acetate not condensed is recovered by scrubbing with propylene and the whole finally distilled.

Vinyl acetate is widely used in vinyl chloride–vinyl acetate co-polymers, and to a lesser extent in ethylene–vinyl acetate co-polymers. It can itself be polymerized by an emulsion process in the presence of a peroxide such as benzoyl peroxide. The emulsion after plasticization with butyl phthalate is a major component in emulsion paints.

Ethylene Oxide

As a consumer of ethylene, ethylene oxide, $CH_2\!-\!CH_2$ (O), comes second in the list.

In the early years of the petroleum chemicals industry ethylene oxide was made by a two-stage process involving the reaction of chlorine and water with ethylene to give chlorohydrin which was then hydrolysed with lime:

$$\text{(a)}\quad CH_2{=}CH_2 + Cl_2 + H_2O \longrightarrow CH_2Cl{-}CH_2OH + HCl$$

$$\text{(b)}\quad 2CH_2Cl{-}CH_2OH + Ca(OH)_2 \longrightarrow 2\,\underset{O}{CH_2{-}CH_2} + CaCl_2 + 2H_2O$$

This procedure posed corrosion problems and consumed large quantities of chlorine and has now given way to direct oxidation of ethylene in the vapour phase:

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \longrightarrow \underset{O}{CH_2{-}CH_2}$$

Much research and development work, in many parts of the world, has gone into this vapour-phase process, mostly with respect to the catalyst used to promote the reaction, which is remarkable, if not unique, in that there is only one substance, i.e. silver, that has any appreciable effect on its rate. Silver, as the principal catalyst component, is one of the few features common to the many plants producing ethylene oxide. The silver is mounted on a variety of supports, and other metal oxides are frequently added with the objective of boosting performance. Reaction efficiency is further improved by the addition of a minute proportion of a chlorine compound, such as ethylene dichloride, to the feed to the reactor. Multitubular reactors, with about 1-in diameter reactor tubes are used, and the heat transfer medium may be Dowtherm, since the temperature is only about 250°C. The hot Dowtherm is used to raise steam.

In one version of the process ethylene and air are added to recycle gas to give a mixture containing about 2 per cent ethylene as reactor feed (Fig. 9). Per pass the conversion is about 30 per cent at 70 per cent selectivity. Ethylene oxide is scrubbed out of the exit gas with water, and the greater part of the scrubbed gas is recycled. The rest passes to a second reactor run at a higher temperature to give about 80 per cent conversion at 50 per cent selectivity. Ethylene oxide is distilled from the aqueous scrubber liquid. Purification presents no problems, since the products of reaction are almost entirely ethylene oxide, CO_2 and

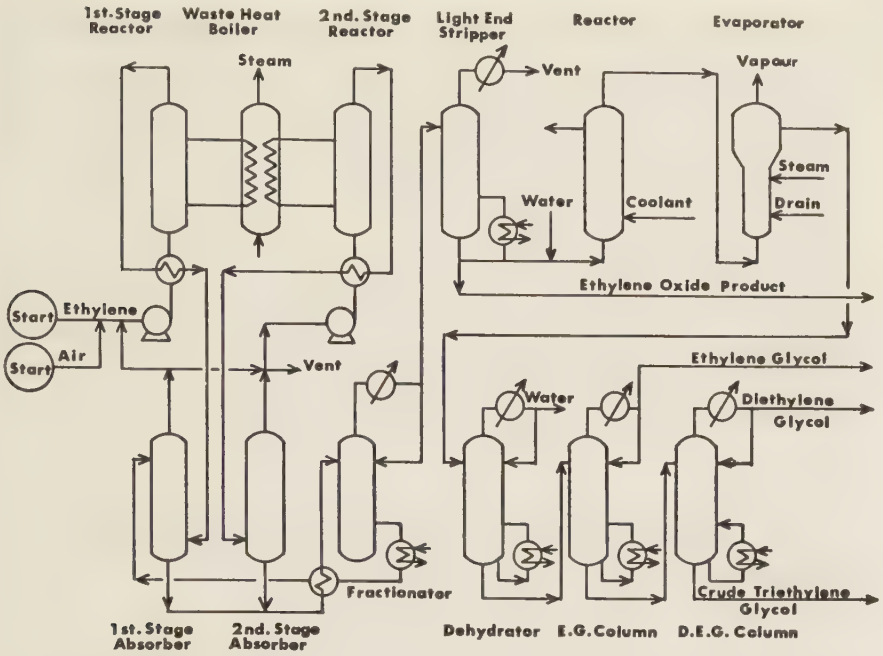


FIG. 9. Ethylene oxide and ethylene glycols from ethylene. (Courtesy of *Hydrocarbon Processing*.)

H_2O. Usage of ethylene in a plant such as this would be about 1 ton per ton of pure ethylene oxide recovered.

In recent years there has been a tendency towards the use of pure oxygen for the vapour-phase oxidation of ethylene. This is now always likely to be used in newer plants as the yield of ethylene oxide is increased. The main use of ethylene oxide is in the production of ethylene glycol. In some plants the two stages are integrated, thereby effectively converting ethylene directly to ethylene glycol. Ethylene oxide is hydrated to ethylene glycols in the liquid phase at 50–70 °C at atmospheric pressure, usually in the presence of an acid catalyst. Some diethylene glycol and triethylene glycol are formed and separated from water and monoethylene glycol by a somewhat complex distillation system (Fig. 9).

In a recently developed process ethylene glycol can be produced directly from ethylene; the latter in acetic acid solution is treated with oxygen at 28 atm in the presence of tellurium oxide and a bromide. The products are ethylene glycol mono (and di-) acetate, both of which are readily hydrolysed to ethylene glycol, the advantage being that negligible di- or tri-ethylene glycols are formed.

Other uses of ethylene oxide are the production of non-ionic detergents by reacting with alkyl benzenes (see below), of ethanolamines by reacting with ammonia, and glycol ethers by reacting with alcohols. Another major use is in the production of polyurethane foams (see below).

The traditional market for ethylene glycol has been as an anti-freeze in car

radiators, but in recent years its use for the production of polyester film and fibre has been rapidly catching up (see below). Diethylene glycol and triethylene glycol both have uses in the drying of natural gas, as humectants, and in the manufacture of unsaturated polyesters. Diethylene glycol can be used in the extraction of aromatics by the Udex process. The ethers of the glycols are mainly used as solvents with high solvent power, and in brake fluids.

Ethylene Dichloride

This is made by chlorination of ethylene either in the vapour phase in the presence of ferric chloride at about 100–110°C or, more usually, in the liquid phase in the presence of ferric chloride and ethylene dichloride, itself, as a solvent, and at a temperature of 50°C. Reaction of ethylene dichloride with ammonia gives ethylene diamine, useful as a basis for sequestering agents, but by far the greater part of ethylene dichloride is converted into vinyl chloride.

Vinyl chloride

Cracking of ethylene dichloride at 550°C yields vinyl chloride and hydrochloric acid:

$$CH_2Cl—CH_2Cl \longrightarrow CH_2—CHCl + HCl$$

Modified Deacon's processes were used to re-oxidize the hydrochloric acid, but these have now generally been integrated into the cracking process so that, in principle, oxygen and ethylene dichloride give, ultimately, vinyl chloride and water. The ethylene dichloride is often not isolated and the reaction becomes the reaction between ethylene, oxygen, and hydrochloric acid to yield vinyl chloride and hydrochloric acid the whole then being repeated. In the liquid-phase process it is possible to carry out both stages in the same reactor.

Polyvinyl chloride

This is produced from vinyl chloride by either suspension, emulsion, or bulk processes. Suspension processes are most used, mechanical agitation of the vinyl chloride with water in the presence of a vinyl chloride-soluble initiator. In emulsion polymerization vinyl chloride, water, an emulsifier, and a water-soluble initiator are mixed and subjected to vigorous agitation. A latex is formed, useful itself for some applications, but usually the PVC is precipitated by addition of an electrolyte.

After compounding with stabilizers, lubricants, etc., the PVC can be extruded 'rigid' or it can be blended with up to an equal weight of a high-boiling ester such as diethyl hexanol phthalate (see below), when it becomes flexible and can be sheeted, moulded, or extruded. The major use of rigid PVC is in pipe, conduit, and fittings, as well as in building construction, while the plasticized variety is used in flooring, cable insulation, and house furnishing.

Ethylene Dibromide

Ethylene dibromide can be made by a process analogous to ethylene dichloride and is a scavenger for lead from the tetraethyl lead used in gasoline.

Ethylene–Propylene Rubbers

These could be considered either modified ethylene derivatives or modified propylene derivatives, but as they frequently contain 55 per cent ethylene they will be considered here. Besides propylene they contain about 5 per cent of a diene to enable vulcanization to be carried out. Such dienes are 1,4 hexadiene or ethylidene norbornene. Polymerization is carried out at about room temperature at approximately 5 atm in the presence of a catalyst such as aluminium alkyl-vanadium. Although the cheap principal raw materials and the low density of the rubber (0.87 g/ml) should make these very attractive they never seem to have fulfilled their early promise. Very little has been used in tyres and then only in tyres for special purposes. In general applications, there has been some replacement of SBR, BR, and neoprene rubbers.

Ziegler Olefins and Alcohols

By treating ethylene with aluminium trialkyls at high pressures either higher straight-chain alcohols or straight-chain olefins can be produced according to the reaction conditions. These are of great value in biodegradable detergents.

DERIVATIVES OF PROPYLENE

Polypropylene

Although growth is only at a modest level now the manufacture of polypropylene grew at an astonishing rate and by 1980 had reached 5 MM tonnes world-wide, so it is now one of the major thermoplastics. It is made by a procedure very similar to that for high-density polyethylene; in fact, some plants have been constructed to make either according to the demand. As catalyst aluminium alkyls are frequently used in conjunction with titanium trichloride. It is essential that very pure propylene be used. Both isotactic (stereo regular) and atactic (irregular form) are produced, and many attempts have been made, with some success, to keep production of the atactic form as low as possible. A very important stage in the production is to reduce the amount of the atactic polymer, which is done by extraction with a hydrocarbon or halocarbon solvent. The catalyst residues must also be removed, and this can be done by treating them with alcohols and thus producing soluble products which can then be extracted as solutions.

Polypropylene is more rigid and more temperature-resistant than HDPE. Articles made from it can be sterilized. Its chief disadvantage is its increasing brittleness as the temperature is lowered. This can be largely overcome, either by adding about 5 per cent of ethylene to the propylene before polymerization or by blending after polymerization with a small quantity of butyl rubber or ethylene–propylene rubber. Polypropylene does oxidize readily and anti-oxidants must be added before the polymer is exposed to the air.

It has found an enormous number of uses, the major applications have been in injection moulded products and products from fibre or filament. There is also a considerable quantity of polypropylene film made which, after stretching and drawing, forms a very tough product.

Butyraldehyde and the OXO Reaction

Hydrogen and carbon monoxide (synthesis gas, water gas) react with olefins in the presence of a catalyst in the following way:

$$R_1R_2C{=}CR_3R_4 + CO + H_2 \longrightarrow R_1R_2C(CHO){-}CHR_3R_4 \text{ and } R_1R_2CH{-}CR_3R_4(CHO)$$

This is known as the OXO or hydroformylation reaction, and its chief industrial application is in the production of butyraldehydes from propylene. According to the earlier versions of the process hydrogen and CO (mol ratio 1) and propylene, together with a dissolved cobalt catalyst, introduced as the metal or a cobalt salt which becomes converted to cobalt carbonyl, are heated under a pressure of two or three hundred atmospheres at a temperature of 150°–200°C in a continuous-flow reactor. The reaction takes place in the liquid phase (consisting mainly of the aldehydic reaction product), requires a residence time of one or more hours, and yields a mixture of n- and isobutyraldehydes in the ratio of 80/20. Purification of the products includes precipitation of the cobalt, either by addition of a suitable reagent or by thermal treatment, and the separation of the aldehyde isomers by fractional distillation.

Much of the n-butyraldehyde so produced is converted, by condensation in the presence of alkali catalyst, to 2-ethylhexenal which is then hydrogenated to 2-ethylhexanol:

$$2CH_3{-}CH_2{-}CH_2CHO \xrightarrow{\text{NaOH catalyst}}$$

$$CH_3CH_2CH_2{-}CH{=}C(CH_2CH_3){-}CHO \xrightarrow{H_2} CH_2CH_2CH_2{-}CH_2{-}CH(CH_2CH_3){-}CH_2OH$$

The phthalic ester of 2-ethylhexanol is a major plasticizer for PVC. Other important outlets for n-butyraldehyde are in the manufacture of n-butanol (solvent, n-butyl esters) and cellulose acetate butyrate.

A Shell process uses cobalt salts of organic acids, trialkyl phosphorus and an alkali as catalyst precursors. These are fed to the reactor and the catalyst proper formed *in situ*. This catalyst is more thermally stable, so lower pressures can be used and higher temperatures, but the reaction is slower. The alcohols are produced directly with a rather more favourable normal/iso ratio. Then aldol condensation can, if desired, take place in the same reactor, so that 2-ethyl hexanol is formed directly from propylene, carbon monoxide, and hydrogen.

Still lower pressures can be used by substituting rhodium for cobalt and the use of complexes involving rhodium carbonyls and triphenyl phosphine.

The OXO reaction is also applied to higher olefins, in particular to those in the C_7–C_9 range, to give (after hydrogenation) C_8–C_{10} alcohols which, similarly to 2-ethylhexenal, are used in plasticizer manufacture. The quality of the dialkyl phthalate plasticizers depends on the configuration as well as the size of the alkyl groups; materials containing highly-branched alkyl groups are, in general, inferior.

Isopropyl Alcohol and Acetone

The hydration of propylene is similar to that of ethylene. Both the two-stage liquid and the vapour-phase processes are used. More than half the isopropanol made is converted to acetone by dehydrogenation:

$$CH_3CHOHCH_3 \longrightarrow CH_3COCH_3 + H_2$$

Besides the production of acetone the main use of isopropyl alcohol is as a solvent. It is free from many of the excise restrictions applicable to ethyl alcohol.

Its low melting point ($-88.5°C$) makes it useful in preventing carburettor icing and as a de-icing material in many applications.

Another major source of acetone is the cumene → phenol process which is described later. Acetone is also made by direct oxidation of propylene in a further application of the Wacker process:

$$CH_2{=}CHCH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_3COCH_3$$

Acetone is a raw material in the manufacture of methyl methacrylate, the tough transparent polymer from which, for instance, aeroplane windows are made (see above). Acetone is, itself, a useful low-boiling solvent, but by further condensation can produce a range of excellent medium/high boiling solvents.

$$2CH_3COCH_3 \xrightarrow[\text{alkali}]{} \underset{\text{Diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3} \xrightarrow[\text{acid}]{}$$

$$(CH_3)_2C{=}CHCOCH_3 \xrightarrow[\text{catalyst}]{} \underset{\text{methyl isobutyl ketone}}{(CH_3)_2CHCH_2COCH_3} \xrightarrow[\text{catalyst}]{}$$

Mesityl oxide

$$(CH_3)_2CHCH_2CH(OH)CH_3 \xrightarrow[\text{catalyst}]{} \underset{\text{hexylene glycol}}{(CH_3)_2C(OH)CH_2CH(OH)CH_3}$$

methyl isobutyl carbibol

Propylene Oxide

Here the propylene is reacted with chlorine and water to give propylene chlorhydrin which with alkali gives the oxide:

$$CH_2{=}CHCH_3 + HClO = CH_2ClCH(OH)CH_3$$

$$CH_2ClCH(OH)CH_3 + NaOH = \underset{\diagdown\,O\,\diagup}{CH_2{-}CHCH_3} + NaCl$$

Recently, however, direct oxidation processes have been developed as already mentioned under ethyl benzene. As an alternative isobutane can be peroxidized and reacted with propylene to give propylene oxide and tertiary butyl alcohol, the latter giving useful results as an anti-knock blending agent in gasoline, while it is also a source of isobutylene:

$$CH_3CH(CH_3)_2 = \underset{\text{Isobutane peroxide}}{CH_3C(CH_3)_2OOH}$$

$$CH_3C(CH_3)_2OOH + CH_2{=}CHCH_3 = \underset{\diagdown\,O\,\diagup}{CH_2{-}CHCH_3} + (CH_3)_3COH$$

Much of the propylene oxide is converted to propylene glycol, which in some applications has the advantage of being less toxic and less corrosive than ethylene glycol. The main use is in the production of polyurethane foams (see below).

Acrylic Acid and Esters

While much acrylic acid is still made from acetylene via the Reppe process, production from propylene is growing either via acrolein or in a single-stage oxidation process. Conversion to acrolein takes place by reacting propylene with air in the presence of a solid catalyst, e.g. bismuth and molybdenum or uranium in the vapour phase at 425–510°C, and usually at just above atmospheric pressure. The acrolein can then be oxidized to acrylic acid in a vapour-phase reaction over cobalt molybdate. Demand for acrolein is, however, limited (menthione is its only important industrial derivative), so most processes recently developed concentrate on producing acrylic acid from propylene in one step. Thus propylene, steam, and air are passed over metallic oxide catalysts at 400°–500°C. Some acrolein is formed, but this can be recycled.

The most valuable products of acrylic acid are its esters which are made by conventional means.

The esters of acrylic acid are used, above all, in the manufacture of emulsion paints. Methyl acrylate is co-polymerized in minor proportion with acrylonitrile to facilitate dyeing of the polymer. Thermosetting acrylic finishes of cars and domestic appliances are increasingly popular. The many smaller applications include adhesives and textile and leather finishes.

Acrylonitrile

Acrolein reacts with ammonia and molecular oxygen in the vapour phase over molybdic oxide and other catalysts to yield acrylonitrile:

$$CH_2{=}CHCHO + NH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_2{=}CHCN + 2H_2O$$

In order to produce acrylonitrile from propylene, however, it is not necessary to isolate acrolein, neither is it necessary to use two reactors as for acrylic acid production because both component reactions, i.e. the oxidation of propylene to acrolein and the conversion of the latter to acrylonitrile, occur at convenient rates at the same temperature (420°–480°C) over certain catalysts, while the velocity constant of the second reaction is so much greater than that of the first that acrylonitrile is obtained in good yield with only a small proportion of acrolein. Bismuth phosphomolybdate and various binary oxide mixtures containing antimony oxide have been described as practical catalysts for the overall reaction:

$$CH_2{=}CH.CH_3 + NH_3 + 1\tfrac{1}{2}O_2 \longrightarrow CH_2{=}CH.CN + 3H_2O \qquad \Delta H = -130\,\text{kcal.}$$

Feed to the reactor usually contains 5–8% v/v propylene, an approximately equimolar quantity of ammonia, and 10–30 per cent steam, the remainder being air. Steam helps to retard side reactions such as that of ammonia with

oxygen. Some plants use fluidized-bed reactors, others multitubular fixed beds with molten salt as heat transfer medium. Ammonia is removed from the exit gas by scrubbing it with hot dilute sulphuric acid. Acrylonitrile and other organic products are then washed out of the gas with cold water, and the aqueous solution so obtained is stripped to give concentrated crude product, further fractional distillations of which result in acrylonitrile at about 99.9 per cent concentration (not taking account of added inhibitors of polymerization) and hydrogen cyanide by-product of almost equal purity.

Propylene has almost entirely replaced other feedstocks for acrylonitrile manufacture. The price of the monomer fell dramatically when propylene was introduced in the early 1960s, and subsequently polyacrylonitrile, usually called Acrylic, has become one of the major synthetic fibres. Other, subsidiary, outlets for acrylonitrile are the plastics made by its co-polymerization with styrene alone and with styrene and butadiene, and the oil-resistant rubber acrylonitrile-butadiene. A more recent application of acrylonitrile is its reductive dimerization, by electrolysis, as practised by Monsanto.

$$2CH_2CHCN \longrightarrow CN{-}CH_2{-}CH{=}CH{-}CH_2CN \xrightarrow[2e]{2H^+} CN{-}CH_2.CH_2.CH_2{-}CH_2.CN$$

It is understood that a major growth in the use of this reaction has taken place. The product of this reaction, adiponitrile, may be converted by hydrogenation to hexamethylenediamine, which is one of the constituents of Nylon 66 (see below).

Hydrogen cyanide is an important by-product of the reaction of propylene with ammonia and oxygen, amounting to perhaps one-tenth by weight of the main product, acrylonitrile. This has almost entirely replaced the route from methane and ammonia mentioned earlier.

Glycerol

Several routes to glycerol, all starting from propylene, have been described. We shall mention only two: the oldest, which is still in use, and one of the latest to be developed.

The first process depends on the fact that at a sufficiently high temperature (approx. 500°C) and in the absence of added catalyst, chlorine does not add on to propylene but substitutes in the methyl group, yielding allyl chloride:

$$CH_2{:}CHCH_3 + Cl_2 \longrightarrow CH_2{:}CHCH_2Cl + HCl\,(-28\,kcal)$$

The allyl chloride, condensed at low temperature from the reactor exit gas, is separated by fractional distillation from unwanted isomeric by-products, and is then treated with hypochlorous acid to produce the dichlorohydrin:

$$CH_2{:}CHCH_2Cl + HOCl \longrightarrow CH_2Cl{-}CHOH{-}CH_2Cl$$

Hydrolysis is now brought about, in two stages the first with the aid of a lime/water slurry to give epichlorohydrin (also used in the production of epoxy resins (see below)).

$$CH_2Cl{-}CHOH{-}CH_2Cl \longrightarrow CH_2Cl{-}\underset{\diagdown\,O\,\diagup}{CH}{-}CH_2 + HCl$$

Epichlorhydrin reacted with sodium hydroxide solution at above 100°C yields glycerol:

$$CH_2Cl—\underset{\diagdown\,O\,\diagup}{CH—CH_2} + 2H_2O \longrightarrow CH_2(OH)—CH(OH)—CH_2(OH) + HCl$$

The second process starts with the oxidation of propylene to acrolein which on reaction with isopropanol over a magnesia catalyst gives allyl alcohol and acetone:

$$CH_2{=}CHCHO + CH_3—CH(OH)—CH_3 \longrightarrow CH_2{=}CHCH_2(OH) + CH_3—CO{=}CH_3$$

Transfer of hydrogen from isopropanol to acrolein is more efficient than direct hydrogenation of the latter, which tends to saturate the double bond.

Upon reaction with warm aqueous hydrogen peroxide solution in the presence of tungstic acid as catalyst allyl alcohol yields glycerol, which is purified by vacuum distillation:

$$CH_2{=}CHCH_2(OH) + H_2O_2 \longrightarrow CH_2(OH)—CH(OH)—CH_2(OH)$$

Synthetic glycerol is made on a large scale in the USA but not in the UK, where the replacement of soap (in the manufacture of which glycerol is a by-product) by detergents has been less extensive. Glycerol is used in the manufacture of alkyd resins (principally), as a plasticizer in cellophane, and in the preparation of tobacco and many toilet commodities.

For the use of propylene in the production of phenol see under benzene.

DERIVATIVES OF BUTADIENE AND THE BUTENES

There are not many processes in which the butenes and butadiene undergo chemical transformation other than by polymerization. Much of the n-butenes separated for synthesis purposes is converted to butadiene, more than 90 per cent of which is consumed in the manufacture of styrene-butadiene rubber (the original synthetic rubber—still of paramount importance) and polybutadiene rubber. The discovery, in the early 1950s of the polymerization of isoprene,

$$\begin{array}{l} \quad CH_3 \\ \quad | \\ CH_2{=}C—CH{=}CH_2 \end{array}$$

to *cis*-1,4-polyisoprene, which is the structure of natural rubber, caused, at least temporarily, some doubts as to the future of butadiene in synthetic rubber manufacture. It now appears that butadiene-based rubber is not threatened by isoprene, because the cost of producing isoprene still exceeds that of butadiene, styrene, etc., while the butadiene-based rubbers have some technical advantages over natural rubber for many applications.

The principal rubbers from butadiene and isobutene are given below. It must be appreciated, however, that there are many variations in the raw material composition, additives and conditions of polymerization, and only a very brief outline of each rubber can be given.

Styrene-butadiene (SBR)

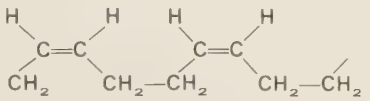
Made by emulsion polymerization of a mixture of 25 per cent styrene and 75 per cent butadiene at about 5 °C and a redox catalyst, e.g. an inorganic persulphate and ferrous sulphate. Unreacted butadiene and styrene are removed and recirculated, an anti-oxidant added and latex (unless latex is the required end product) coagulated, e.g. with acid sodium chloride, and the rubber 'crumb' filtered, washed, and baled. An important modification is an oil-extended rubber where an emulsion of a heavy oil is added to the latex before coagulation.

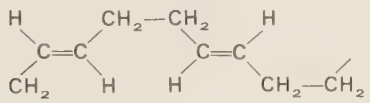
SBR is compounded with ingredients broadly similar to natural rubber, e.g. reinforcing agents, anti-oxidants, softeners, and vulcanization agents.

Its main use is in passenger car tyres where it has better abrasion resistance than natural rubber. It can be used, however, in almost all natural rubber outlets and it is often solely a question of economics which rubber is used for any particular application. The greater consistency of SBR compared to natural rubber has won it some markets, and in general it appears slowly to be gaining ground at the expense of natural rubber.

Polybutadiene (BR)

Here the polymer is required substantially in the cis-form as the trans-form is thermoplastic and cannot be cured.





This is achieved by stereospecific catalysts such as trialkyl aluminium and a titanium or cobalt compound. Normally the polymerization is carried out in a cyclohexane solution at slightly above room temperature.

Its main use is in truck tyres, normally in combination with GRS or natural rubber. A small but important use is in the production of high-impact polystyrene (see above).

Butyl rubber

This is a copolymer of isobutene with 2–5 per cent isoprene. It is obtained by solution polymerization at a very low temperature, e.g. −100 °C in the presence of a Friedel–Crafts catalyst. A slurry of small rubber particles is produced, solvents and unreacted hydrocarbons are flashed off, antioxidants and zinc stearate are added and, after vacuum stripping, the rubber crumb is produced. It can be vulcanized with sulphur, like natural rubber and SBR, but needs very active accelerators and a high temperature, 190 °C. The unique property of butyl rubber is its extreme impermeability to gases and, properly compounded, its resistance to ageing. It is very resistant to many chemicals. Its

main use has been in inner tubes for tyres, but this application is now declining. It has some use in cable insulation, in tank linings, chemical plant hose, and a few other applications for which its special properties justify it. It is, however, not compatible with natural rubber or SBR.

Two other special synthetic rubbers from butadiene are nitrile (NBR) and chloroprene rubber (Neoprene). The first is made by broadly similar methods to those used for SBR, by polymerization of two-thirds butadiene and one-third acrylonitrile. The monomer for the second is produced by the chlorination of butadiene, the isomerization of the mixed isomers produced to 3,4-dichlorobutene-1, and dehydrochlorination of the latter to chloroprene, $CH_2{=}CCl.CH{=}CH_2$. Emulsion polymerization then gives chloroprene rubber. Both these speciality rubbers are used where their oil-resistant properties are needed, and chloroprene also because of its heat resistance.

Polyisobutenes are being made, on an increasing scale, in various molecular weight ranges. They are used as lubricating oil additives, sealing compounds and adhesives, and have many minor applications.

With methyl alcohol isobutene yields methyl tertiary butyl ether, a valuable anti-knock blending agent in gasoline.

The hydration of the n-butenes, via butyl hydrogen sulphate, is similar to that of ethylene and propylene:

$$\begin{matrix} CH_3CH_2CH{=}CH_2 \\ \text{or} \\ CH_3CH{=}CHCH_3 \end{matrix} \xrightarrow{H_2SO_4} CH_3CH_2\underset{\displaystyle OSO_2OH}{\underset{|}{C}}HCH_3 \xrightarrow{H_2O} CH_3CH_2CHOHCH_3$$

but the feed to the process is usually a mixture of butenes and butane from which the butenes are selectively absorbed in the sulphuric acid.

Most of the product of the process, sec-butanol, is dehydrogenated to methyl ethyl ketone:

$$CH_2CH_2CHOHCH_3 \longrightarrow CH_3CH_2COCH_3 + H_2$$

Both the alcohol and the ketone are solvents, but the ketone is much the more important.

On oxidation n-butene yields maleic anhydride on a fixed- or fluid-bed, using vanadium pentoxide as a catalyst and at a temperature of 350–400 °C. Butane or a mixture of butane and n-butenes can also be used. This process compares very favourably with the older one based on the oxidation of benzene which it has largely displaced.

The reaction is strongly exothermic and arrangements must be made to remove the heat evolved. It can be carried out either on a fixed-bed or a fluid-bed. The crude product is collected and maintained at 280 °C to decompose any by-products and then purified by distillation.

DERIVATIVES OF CYCLOHEXANE AND THE AROMATIC HYDROCARBONS

It is convenient to group together the derivatives of cyclohexane, benzene, toluene, the xylenes, cumene, and naphthalene, since in most instances two or more alternative feedstocks from this group are used for the same product.

We consider first the products of the catalysed vapour-phase oxidation of aromatics. When there are alkyl groups attached to an aromatic ring they are oxidized preferentially. Toluene will yield benzaldehyde or benzoic acid, according to the severity of oxidation, and the three xylenes will yield, more or less, the corresponding dibasic acids, or, in the case of the ortho, the anhydride.

The oxidation of *o*-xylene, because of the proximity of the two carboxyl groups that are first formed, results in phthalic anhydride. If, however, there are no groups on the ring or if oxidation is more intense, the ring is opened, there is partial destruction (by formation of carbon oxides) of the two ends of the chain thus exposed, and a stable anhydride is again produced. Thus benzene, by vapour-phase oxidation, yields maleic anhydride, and naphthalene yields phthalic anhydride.

The preparation of maleic anhydride from benzene has already been mentioned under butenes.

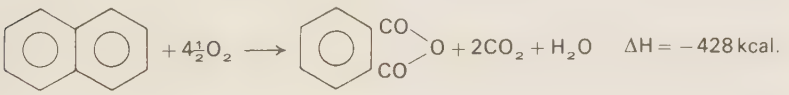
The principal use of maleic acid is in the manufacture of polyesters, and amongst the various minor outlets are plasticizers and surface-coating materials. In some applications, where cross-linking is required, it has an advantage over phthalic anhydride.

Phthalic Anhydride

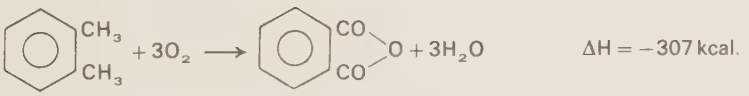
This substance has been manufactured for over seventy years, originally as a dyestuffs intermediate. Nowadays the increasingly large output is used almost exclusively in the manufacture of plasticizers (chiefly for PVC), alkyd resins, and polyester resins. Originally the feedstock for its manufacture was naphthalene derived from coal, but this is now insufficient and petroleum-based naphthalene and *o*-xylene, particularly the latter, are used.

The principle, common to all the various phthalic anhydride processes, is that the hydrocarbon feed is vaporized, mixed with air, and passed over a vanadium-containing catalyst at high temperature, e.g. 350°C.

With naphthalene the reaction is:



and with *o*-xylene:



The main side reaction is that of complete combustion to CO_2 and H_2O.

The very large heat output of the reaction necessitates either a fixed-bed multitubular reactor or a fluidized bed. Tubes in the fixed-bed are 1-inch diameter or less, and they are cooled by the circulation of molten salt, usually a mixture of sodium nitrite and potassium nitrate. Heat removal is facilitated by the use of a fluidized bed, but this too may have its problems and, in particular,

that of after-burning, i.e. the uncontrolled reaction on catalyst inevitably carried over from a fluidized bed and deposited subsequently on a surface not provided with heat transfer means. Avoidance of after-burning requires abrupt, efficient quenching of reactor effluent gas.

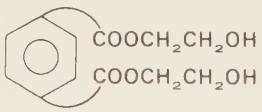
The crude product is collected from the reactor exit gas stream in switch condensers that are alternately cooled for trapping the anhydride and heated so that it may be melted and run off. Purification typically consists in first maintaining the crude material at a temperature of about 280°C for several hours in order to decompose or polymerize reactive by-products that would otherwise be difficult to eliminate by distillation. Topping and tailing distillation procedures carried out at reduced pressure then eliminate the impurities.

m-Phthalic Acid

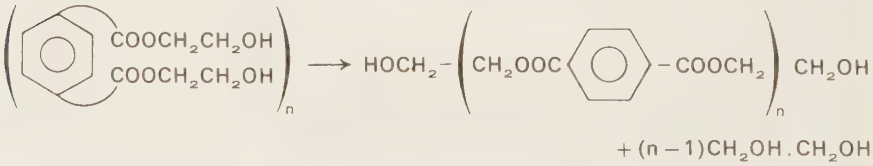
Made by the oxidation of *m*-xylene in the liquid phase at 190°C and 50 atm pressure by oxygen in acetic acid in presence of cobalt acetate. When the higher cost permits it can advantageously replace phthalic anhydride in, e.g. medium and long oil alkyds to give faster drying paints which at the same time form tougher but flexible films. Unsaturated polyesters made with isophthalic acid instead of phthalic anhydride show higher heat resistance, higher strength, and lower water absorption.

Terephthalic Acid

The ethylene glycol ester of terephthalic acid, di-(2-hydroxyethyl) terephthalate



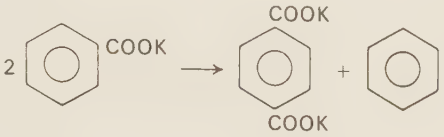
when heated under reduced pressure gives the condensation polymer polyethylene terephthalate, with elimination of glycol:



This is the polyester used in the manufacture of films and fibres bearing well-known brand names such as Terylene and Dacron. There are several processes for the polyester production, in some of which the simple glycol ester is not isolated, and some in which terephthalic acid does not appear in its free state.

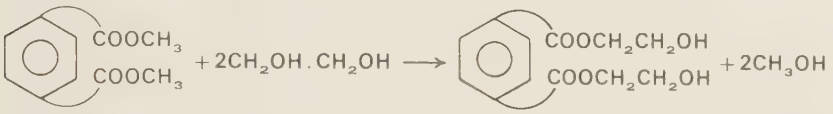
Terephthalic acid may be made from toluene, which is oxidized in the vapour or liquid phase to benzoic acid. The potassium salt of benzoic acid

when heated under pressure with cadmium benzoate as catalyst disproportionates to potassium terephthalate and benzene:

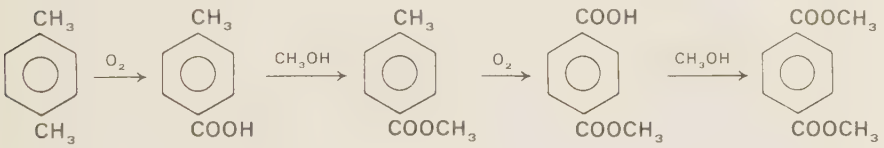


Most terephthalic acid or ester is, however, made from *p*-xylene.

In the earlier days the production of pure terephthalic acid was difficult. Nitric acid was used for a time but has now been abandoned. It was found, however, that the dimethyl ester of terephthalic acid could be readily purified by crystallization from methanol and then reacted with ethylene glycol to form the glycol ester and free methanol, the former readily polymerizing to poly(ethylene glycol terephthalate).



Probably the most widely used process is that which leads to the production of dimethyl terephthalate from *p*-xylene by alternate oxidation and esterification steps.



In the first step liquid *p*-xylene is converted to *p*-toluic acid by contact with air with the aid of a cobalt catalyst. The acid is then esterified by refluxing with methanol and an acid catalyst. Repetition of the oxidation step (under more severe conditions) and further esterification give the dimethyl ester. This lengthy procedure is justified on the grounds that it reduces by-product formation and hence facilitates purification. More cogent is the fact that at the time of its introduction there appeared to be no process for the single-stage oxidation of *p*-xylene to terephthalic acid. Processes have been described according to which the four steps outlined above are carried out simultaneously in a single reactor to which are continuously fed *p*-xylene, air, methanol, and catalyst, with the continuous production of dimethyl terephthalate.

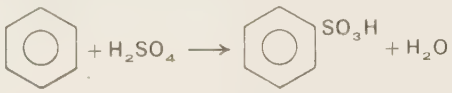
For many years almost all polyester fibres were made from dimethyl terephthalate, but gradually methods were discovered for overcoming the reluctance of *p*-xylene to proceed to terephthalic acid and for its purification. The two chief processes used at present are the oxidation of *p*-xylene in acetic acid by air at 200 °C at a pressure of 20 atm. Cobalt and manganese bromides are used as catalysts, the bromide anion playing a critical part. The other main process uses acetaldehyde or methyl ethyl ketone in the acetic acid as a

promoter. Purification techniques include crystallization from water at high temperatures and pressures, and a process based on sublimation.

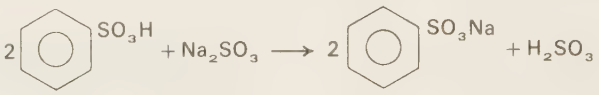
Phenol

The oxidation of benzene to phenol by means of molecular oxygen resembles that of methane to formaldehyde in being obvious, direct, and stoichiometrically simple, but difficult to achieve. It is doubtful if any phenol is made by such a method.

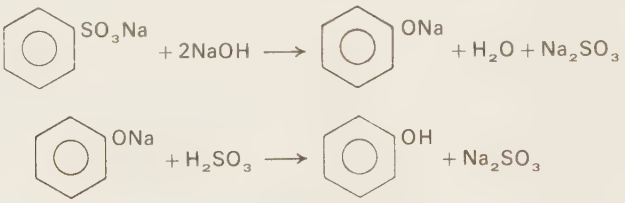
The oldest process begins with the sulphonation of benzene:



The benzenesulphonic acid is then neutralized with sodium sulphite:



Fusion of sodium benzenesulphonate with caustic soda gives sodium phenate, from which phenol is generated by acidification with sodium bisulphite:



Another route is to produce monochlorobenzene by the reaction of chlorine with an excess of benzene (excess restricts the formation of dichlorobenzene) in the presence of iron chloride catalyst at about 70 °C. Purified monochlorobenzene is reacted with caustic soda solution at about 350 °C, under a pressure of 300 atm and from the sodium phenate so obtained phenol is generated by the addition of hydrochloric acid.

Almost all phenol is now made from benzene and propylene. A typical process is to alkylate benzene with propylene in the vapour phase at 250 °C and 25 atm, using a supported phosphoric acid catalyst. The cumene produced is emulsified with dilute sodium carbonate to give, on oxidation with air, the cumene hydroperoxide which on treatment with dilute sulphuric acid at 80 °C breaks down to phenol and acetone. This is a very simplified description, the actual manufacture consisting of many stages in which the various products are purified and the by-products removed. The basic reaction steps are shown below:

$$C_6H_6 + CH_3CH{=}CH_2 \longrightarrow C_6H_5CH(CH_3)_2 \xrightarrow[O_2]{}$$

$$C_6H_5C(OOH)(CH_3)_2 \xrightarrow[H_2SO_4]{} C_6H_5OH + CH_3COCH_3$$

Nearly half the phenol produced is reacted with formaldehyde to produce phenolic resins for moulding powders, laminates, and adhesives, while there is a substantial use of phenol for caprolactam manufacture for Nylon 6. Another major use is the reaction with acetone to form diphenylol propane (Bisphenol A), which itself reacts with epichlorhydrin to yield epoxy resins. Diphenylolpropane also reacts with carbon monoxide under special conditions to give polycarbonate resins. There are other small but nevertheless important applications of phenol such as the production of alkyl phenols for, e.g. non-ionic detergents, phenoxyacetic acids for weedkillers, the production of chlorphenols used in herbicides and wood preservatives, while phenol is also used to a considerable extent in the pharmaceutical industry.

The Nylons

The principal raw materials required are adipic acid, hexamethylene diamine, and caprolactam, all of which are benzene, toluene, or phenol derivatives.

Benzene is hydrogenated, either in the liquid or vapour phase to cyclohexane in the presence of a nickel or platinum catalyst. Optimum temperatures and pressures vary according to the exact process used.

Cyclohexane is oxidized with air at 150°C and 10 atm in the presence of a cobalt salt as catalyst to a mixture of cyclohexanol and cyclohexanone. The mixture can itself be oxidized by nitric acid at about 70°C in the presence of a copper/vanadium catalyst to adipic acid.

Adipic acid can be reacted with ammonia in the vapour phase at 280°C in the presence of a catalyst containing boron and a phosphate to yield adiponitrile which, on hydrogenation, gives hexamethylene diamine.

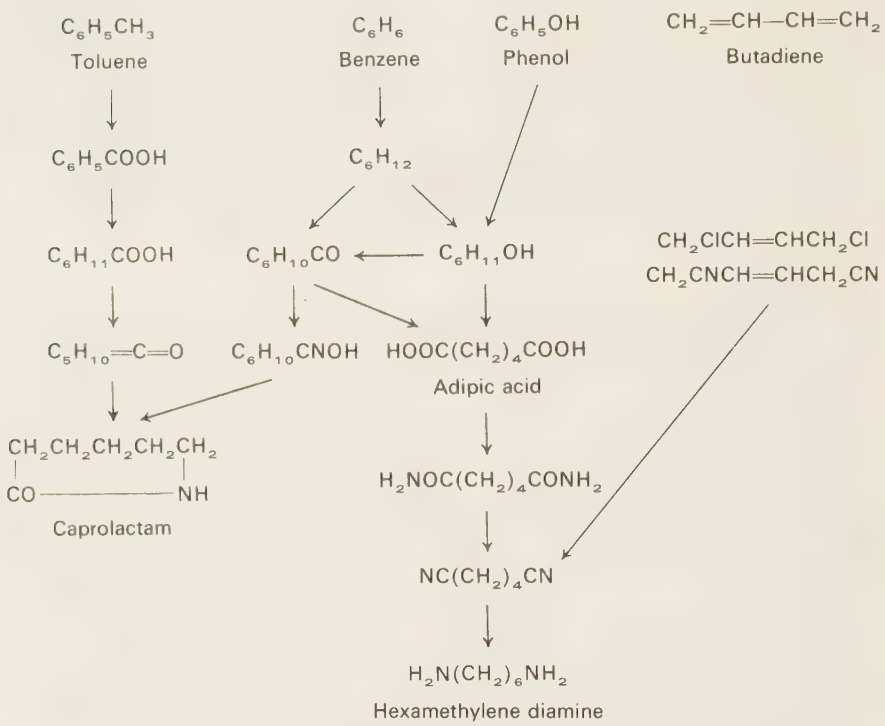
Alternatively, adiponitrile can be prepared from butadiene by chlorination, isolating the 1,4-dichloro-2-butene isomer, treating with hydrogen cyanide and hydrogenating. The route from acrylonitrile can also be used (see above).

The route from phenol involves the hydrogenation of phenol at 150°C and 15 atm to cyclohexanol in the presence of a nickel catalyst. This is reported to be much safer than the oxidation of cyclohexane. The cyclohexanol can be oxidized directly to adipic acid as mentioned above. For caprolactam, however, pure cyclohexanone is required which is obtained by dehydrogenating cyclohexanol using a zinc–iron catalyst at 400–500°C. Starting with the cyclohexanol–cyclohexanone mixture it is usual to separate off the latter first by fractional distillation.

For caprolactam the cyclohexanone is treated with hydroxylamine to give the oxime which then with oleum undergoes the Beckmann rearrangement to give caprolactam. Very large quantities of ammonium sulphate are produced as a by-product, and many attempts, with some success, have been made to reduce this. Probably the most successful is to dilute the strongly acid caprolactam to an acid strength of about 50 per cent, and then add an alkyl phenol which forms a complex with caprolactam which can be separated and broken down, the 50 per cent acid being reconcentrated.

Caprolactam can also be prepared from toluene by oxidizing it to benzoic acid, hydrogenating this to cyclohexane carboxylic acid and dehydrating to pentamethylene ketene. The latter is nitrosated to the oxime, the Beckmann rearrangement being carried out simultaneously.

The various reactions described above are shown diagrammatically below:

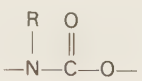


Nylon 6 is produced by the polymerization of caprolactam. Nylon 66 is produced by the condensation of adipic acid with hexamethylene-diamine and then polymerization of the 'nylon salt' so formed.

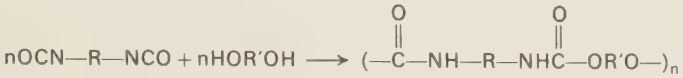
The fibres are produced by extrusion of the respective polymers. Nylon 6 and Nylon 66 are virtually interchangeable, but perhaps with a slight preference for Nylon 6 in fine denier and hosiery type apparel, and Nylon 66 for industrial applications. The production of Nylon 6 is less capital intensive and therefore particularly suited to small plants in developing countries.

Tolylene Di-isocyanates and Polyurethane

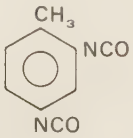
The polyurethanes have many actual and potential applications, including elastomers and surface coatings; their principal use is the manufacture of solid foams. They are polymers whose molecular chains contain the repeated grouping:



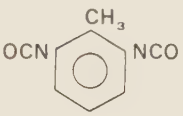
They exist in great variety and many different reagents may be used in their manufacture, but most often they are produced by the reaction of a di-isocyanate with a diol:



The di-isocyanates often used are the two tolylene di-isocyanate isomers:



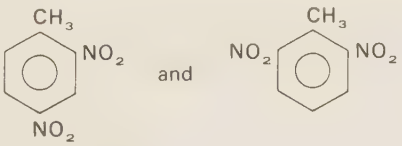
2,4 tolylene di-isocyanate



2,6 tolylene di-isocyanate

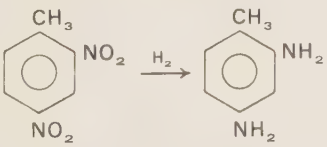
The production of these compounds from toluene involves a lengthy series of operations, with purification procedures complicated by the fact that there are four possible disubstituted toluene isomers in addition to those required. Only the principal features of the process will be mentioned.

Dinitrotoluene is made by the action of nitric and sulphuric acids on toluene. The sulphuric acid increases the rate of reaction and absorbs the water that is formed. The product consists mainly of the 2,4 and the 2,6 isomers:

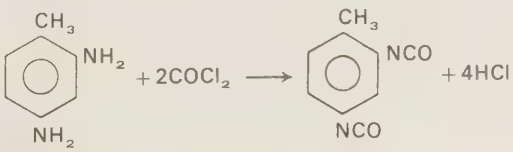


in the ratio of about 4/1, and a small quantity of the other isomers.

In the next stage the nitro groups are reduced to amino groups by hydrogenation under pressure with a catalyst such as palladium:



Phosgene, produced by the simple addition of chlorine to carbon monoxide, converts the diamine into the di-isocyanate:



A wide range of techniques is available for making the foam, but basically the toluene di-isocyanate and the polyol are mixed together with a little water. The first two react and the water causes evolution of carbon dioxide which produces the foam. This is a very simplified description of the whole reaction, but space does not allow for it to be gone into in more detail. Much of the reaction often takes place on a moving band producing a continuous block of foam. The foam can be either flexible or rigid; for flexible foams polyols of moderate molecular weight are used, e.g. mol. wt 3000, whilst for rigid foams highly branched polyols with molecular weights below 1000 are preferred. The diols may be either polyesters or polyethers. Polyesters are often made from adipic acid and glycerol or diethylene glycol, while polyether can be made, e.g. from propylene oxide and glycerol.

It should be mentioned that tolylene di-isocyanate is meeting strong competition from 4-4′ di-isocyanato diphenyl methane and its polymer. These are made from aniline and hence from benzene by nitration and reduction. It is slightly less toxic than the toluene compound, and in Europe is nearly always used in rigid foam.

Polyurethanes by suitable formulation can be used for rubbers, adhesives, and in surface coatings.

Detergents

There have been several mentions of detergent chemicals in this chapter and it was thought helpful to have a summary included.

Useful detergents are made by the cracking of slack wax (see Chapters 16 and 28). This gives mixed olefins in the range C_9-C_{15} which, on sulphation and neutralisation, give the sodium alkyl sulphate, the active detergent. The sulphuric acid reacts preferentially with the alpha-olefins, so that the others can be separated.

Another basic route is to alkylate benzene with higher olefins, sulphonate the product and neutralize it. The preferred olefin for many years was propylene tetramer. It was made by passing propylene over a supported phosphoric acid catalyst at about 220°C and 15–25 atm pressure. The alkylation took place at about 25°C and at 5 atm pressure, using hydrogen fluoride as a catalyst. Sulphonation and neutralization then took place by standard techniques. As detergents began to be more widely used this product was found to be non-biodegradable, and this was traced to the use of branched-chain olefins. The propylene tetramer was therefore replaced by, first partly, and then completely straight-chain olefins. Thus, while olefins obtained by cracking slack wax gave some improvement, to obtain substantially straight-chain olefins one or other of the following procedures have proved the most suitable:

(1) Cracking of straight-chain paraffins obtained from slack wax by the urea adduction process or by a molecular sieve.
(2) Chlorination of straight-chain paraffins produced as in (1), followed either by dehydrochlorination or by direct alkylation of the benzene ring using a Friedel–Crafts catalyst.
(3) Oligomerization of ethylene using a Ziegler catalyst.

Non-ionic, low-foaming detergents were made by condensing ethylene oxide

with alkyl phenols, but these proved to be not very biodegradable, and modern practice is to condense ethylene oxide with straight-chain higher alcohols produced, e.g. from straight-chain olefins by the OXO process (see above). The alcohols can then be sulphated and neutralized.

Modern detergents are made up of blends of many basic active products together with builders: sodium polyphosphate, fillers, and often a per-compound.

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18

Petroleum Gases

By R. H. SHIPMAN and T. G. D. BARNETT

HISTORICALLY much gas has been flared because of its remoteness from consuming markets and the costs involved in transport. However, the growing awareness of the finite nature of the world's hydrocarbon reserves, plus the startling rise in oil prices over the last decade, has made the flaring of such a potentially valuable resource both politically and economically unacceptable. In addition, a growth in the environmental lobby in most developed areas of the world has meant a growing interest in 'clean burning fuels'. Therefore, the attractiveness of a naturally occurring fuel which can be burnt without smoke and is virtually sulphur-free, or can easily be made so, is obvious.

NATURAL GASES

There are two main ways in which natural gas can be found. Broadly they are referred to as 'associated' and 'unassociated' gas. Associated gas is that found in conjunction with a crude oil. The gas is in solution with the other components of the crude oil at the temperature and pressure of the reservoir; there may also be free gas. It is released after production from the well during a process known as crude stabilization. On the other hand, that gas that is found in isolation without any heavier hydrocarbons present is known as unassociated gas; the fields of Groningen or the southern North Sea are good examples of unassociated gas fields.

Both associated and unassociated gas will have methane as their major hydrocarbon constituent. There will be varying amounts of higher hydrocarbons; in general associated gas has a greater proportion of the higher hydrocarbons than unassociated. In addition, there will also be sundry amounts of less desirable components such carbon dioxide, nitrogen, helium, hydrogen sulphide, water vapour, etc. Table I gives a good cross-section of the sort of compositions that can be expected for natural gases from a variety of sources. Obviously the way in which the impurities are treated will depend, to a large extent, on the ultimate use of the gas and the type of market in which it is being sold. Helium, for instance, is normally removed as it is of value in its own right. Hydrogen sulphide is removed because it is both corrosive and toxic, as are its products of combustion. Water vapour is a problem because of the solid hydrates that are formed at low temperature; this is particularly dangerous where the gas is being liquefied for transport or storage. Normally, the inert components, mainly nitrogen and carbon dioxide, will not be touched. This makes it difficult to quote typical figures for the thermal value for natural gas as it can vary from, say, 650 Btu/ft^3 for gas from the Kapuni field of New Zealand to 1954 Btu/ft^3 from gas from the Forties field in the North Sea.

Traditionally gas consumption (see Table II) has largely been in the same place as gas production (see Table III), either as unassociated gas or as a result

TABLE I

Typical Compositions of Various Natural Gases, both Associated and Unassociated

Source	Unassociated gas				Associated gas		
	Australia N.W. Shelf	Algeria Hassi-R'Mel	New Zealand Kapuni	North Sea West Sole	Abu Dhabi Zakum	North Sea Forties	North Sea Brent
N_2	1.0	6.1	1.0	1.2	0.7	1.2	0.9
CO_2	3.2	0.2	44.9	0.5	2.3	0.7	0.9
H_2S	—	—	—	—	0.6	—	—
CH_4	85.3	83.5	46.2	94.3	72.0	46.5	74.0
C_2H_6	5.8	7.0	5.2	3.1	13.9	13.2	12.4
C_3H_8	2.0	2.0	2.0	0.5	6.5	19.8	7.5
C_4H_{10}	0.8	0.8	0.6	0.2	2.6	10.6	2.9
$C_5H_{12}+$	1.9	0.4	0.1	0.2	1.4	8.0	1.4

of gas produced during normal refinery operations. However, the proven reserves in the USA, with the exception of Alaska, are on the decline with no corresponding wane in demand. In addition, the increase in demand for gas in Japan has outstripped that of any other consumer in the non-communist world. Therefore, by reference to Table IV, which shows published proven reserves, it can be seen that, in the next decade, a fundamental change will take place in the world gas market. This will involve transport of considerable amounts of natural gas from producing areas—particularly the Middle East and North Africa—to areas of consumption, North America, Japan, and Western Europe.

Transport of Natural Gases

The simplest and most familiar way for transporting large volumes of gas is by pipeline. In many developed countries extensive pipeline systems have existed

TABLE II

World Consumption of Natural Gas—1981

	Million tonnes oil equivalent	Billion cubic metres	%
USA	509.3	565.8	38.2
USSR	353.7	393.0	26.5
Eastern Europe	69.4	77.1	5.2
Latin America	54.4	60.4	4.1
Canada	48.1	53.4	3.6
United Kingdom	42.0	46.7	3.2
West Germany	41.2	45.8	3.1
Netherlands	28.8	32.0	2.2
France	24.7	27.4	1.9
Japan	24.2	26.9	1.8
Italy	22.8	25.3	1.7
Others	113.4	126.0	8.5
	1 332.0	1 479.8	100

Source: *BP Statistical Review of World Energy*—1981.

TABLE III
World Production of Natural Gas—1981

	Million tonnes oil equivalent	Billion cubic metres	%
USA	499.2	554.6	36.2
USSR	411.8	457.5	29.9
Canada	68.0	75.6	4.9
Latin America	66.3	73.7	4.8
Netherlands	65.0	72.2	4.7
Eastern Europe	46.3	51.4	3.4
Middle East	38.0	42.2	2.8
United Kingdom	31.9	35.4	2.3
Africa	25.0	27.8	1.8
Norway	22.7	25.2	1.6
West Germany	16.7	18.6	1.2
Others	87.6	97.3	6.4
	1 378.5	1 531.5	100

Source: *BP Statistical Review of World Energy*—1981.

for many years for domestic distribution. They were mostly originally used for manufactured gases but now, as discoveries have proceeded, are being used for natural gas transfer. However, when international transfer of gas is considered there are problems. Obviously very long term contracts are needed to justify the considerable capital investment involved in pipelines. In addition, each country may have different specifications for pipeline design, varying methods for regulating the operation and control, differing means of remunerating pipeline participants. When these difficulties are considered, along with the fact that much of the gas is now to be found in areas with political systems that are volatile, it seems unlikely that there will be a tremendous increase in pipeline capacity for natural gas. Table V shows international gas pipeline

TABLE IV
World 'Published Proved' Reserves of Natural Gas—End 1981

	Trillion (10^{12}) cubic feet	Trillion cubic metres	%
USSR	1 160.0	32.8	39.8
Middle East	761.9	21.6	26.2
Africa	211.7	6.0	7.3
USA	198.0	5.6	6.8
Latin America	176.3	5.0	6.1
Western Europe	152.7	4.3	5.2
Canada	90.5	2.6	3.1
China	24.4	0.7	0.8
Eastern Europe	8.8	0.2	0.3
Others	127.6	3.6	4.4
	2911.9	82.4	100

Source: *BP Statistical Review of World Energy*—1981.

TABLE V
International Pipeline Trade in Gas—1981

Exporter	Importer	1981 throughput Billion cubic metres
Netherlands	West Germany	17
	France	9
	Belgium/Luxembourg	9
	Italy	6
	Switzerland	1
USSR	West Germany	11
	Italy	8
	Czechoslovakia	8
	East Germany	7
	Poland	5
	Hungary	5
	Bulgaria	5
	France	4
	Austria	3
	Finland	1
Norway	United Kingdom	11
	West Germany	9
	France	2
	Belgium	2
	Netherlands	2
Canada	USA	22
Mexico	USA	3
Afghanistan	USSR	3
Bolivia	Argentina	2

trade in 1981, and Table VI shows pipelines pending or being considered. It will quickly be noticed that significantly, when comparing Tables V and VI with Table IV showing reserves, no pipelines to the West operate or are planned from what will be the non-communist major source of supply—namely, the Middle East. This is perhaps not surprising when considering the political problems in the area and the geographical distance between the Middle East and the major areas of consumption. How then will this gas be moved. The most likely, if not only, answer is as LNG, Liquefied Natural Gas, by sea in large heavily insulated ships.

The problem with transporting natural gas, when compared with crude oil, is its low thermal density—about 1/900 that of crude oil. Even with better steels and welding techniques, larger diameters and higher operating pressures, it is

TABLE VI
Pipelines Under Construction or Consideration—1981

1. Algeria to Italy, via Tunisia, with an annual throughput of 12 b m^3; pipeline has been laid; awaiting agreement on pricing.
2. Alaska to USA, via Canada, with an annual throughput of more than 20 b m^3.
3. USSR to West Europe, with an annual throughput of 40 b m^3 (plus additional 10 b m^3 to East Europe).
4. Gas-gathering pipeline from Norwegian sector of North Sea to Norway.
5. IGAT-2 pipeline from Iran to USSR, annual throughput 16 b m^3; project currently shelved.

TABLE VII
Important Temperatures for Hydrocarbon Gases

	Boiling point at atmospheric pressure, °C	Critical temperature, °C
CH_4	−162	−83
C_2H_6	−89	32
C_3H_8	−42	97
iC_4H_{10}	−12	135
nC_4H_{10}	−1	152
nC_5H_{12}	36	197

difficult to transport natural gas economically where source and consumer are separated by large stretches of water. Sensibly the only direction in which to move is to reduce the volume of the gas to be transported, i.e. liquefaction. Many hydrocarbon gases can be simply liquefied by increasing pressure. However, natural gas which is predominantly methane has a critical temperature of −83°C—see Table VII—and when it is above this temperature no amount of pressure will liquefy it. It is, therefore, necessary to cool natural gas to at least −83°C before applying pressure. It is now an economic balance as to whether it is better to cool and pressurize or to refrigerate down to the boiling point of −162°C and store at ambient pressure, thereby being able to use thinner materials but obviously requiring more by way of insulation.

Liquefaction

As previously mentioned, the first processes in a liquefaction plant will be to remove those components of the feed gas that are either valuable, e.g. helium, or could cause difficulty further downstream, e.g. water. The equipment used at this stage will be the normal types of dryers, molecular sieves, etc. commonly found in refineries. The treated gas will then pass through to the liquefaction section of the plant.

Where liquefaction is being carried out so as to provide LNG for peak shaving, i.e. the bulk of the gas is still being carried forward, at lower pressure, into a pipeline distribution system, the expander-cycle is commonly used. This relies on the basic physical fact that gas at high pressure, when expanded through a nozzle without doing work, will be cooled. This cooled gas can then be passed through a heat exchanger, and used to cool further supplies of gas going forward to be expanded. Eventually a small percentage of the gas will be liquefied at the expense of the loss of pressure of the rest of the supplied gas. In practice this system would be energy consuming and it is modified so that the expansion takes place through a turbine driving a compressor. The temperature the gas falls is increased by an amount proportional to the work done and thereby increases the cooling effect in the heat exchangers. Figure 1 shows a simplified diagram of the expander cycle.

More often the liquefaction plant is required to produce LNG for transportation, and therefore all the feed gas, not just a small proportion, is

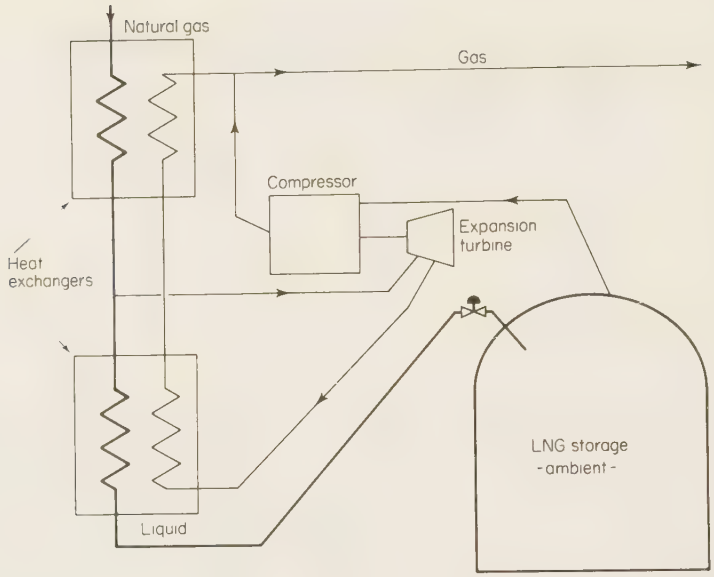

FIG. 1. Simplified diagram of an expander cycle.

required to be liquefied. In this case a form of mechanical refrigeration cycle will be used. The first stage of the process is similar to that of the expander cycles, i.e. the removal of contaminants, etc. The liquefaction stage is, when most simply stated, a straightforward refrigeration cycle. The heat is extracted from the gas to supply the latent heat required to boil the refrigerant. Theoretically the smaller the temperature change in each refrigeration cycle the more thermally efficient is the process, i.e. ideally the liquefying of the gas would take place over an infinite number of stages. Obviously, in practice, capital and maintenance cost of the plant severely limit the number of stages.

Figure 2 shows a simplified version of one type of mechanical refrigeration cycle, which is known as the cascade or multiple-refrigerant cycle. In this system a number of separate refrigeration cycles are used to reduce the natural gas down to $-162^{\circ}C$ in stages. In the example shown the first stage is to reduce the temperature of the gas down to about $-38^{\circ}C$ by using liquid propane as the refrigerant. The second stage reduces the temperature to about $-100^{\circ}C$, with liquid ethylene as the refrigerant. The gas is now cold enough to be liquefied under pressure and the final cooling to $162^{\circ}C$ is by controlled boiling of the liquid methane—in effect the LNG becomes its own refrigerant—so that it can then be stored in a low-pressure LNG storage tank.

In each case the gases produced in the refrigeration process are recirculated through a compressor and water cooled. The propane is liquefied by this process and can be recycled back to the first stage. The ethylene is liquefied by passing it through the propane evaporator prior to being recycled in the second stage. Finally, the methane, after water cooling, is further cooled in the propane evaporator and liquefied in the ethylene evaporator and then recycled into the third stage.

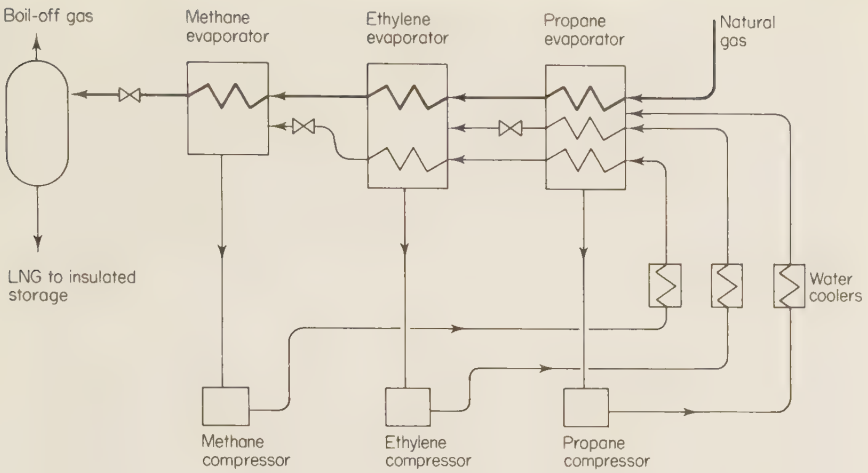

Fig. 2. Simplified diagram of mechanical refrigeration cycle.

Figure 3 also shows a much simplified diagram of a liquefaction system known as the Mixed-Refrigerant Cycle. The main difference between this and the cascade cycle is that a simple mixed refrigerant is used. This is normally a mixture of liquid C_1, C_2, C_3, and C_4 hydrocarbons, plus some condensed nitrogen. It is generally obtained from the condensate knocked out of the natural gas feed during treatment prior to liquefaction.

The operation of the cycle as depicted in Fig. 3 can be explained as follows: Refrigerated vapour is drawn off from the first cooling stage by a compressor

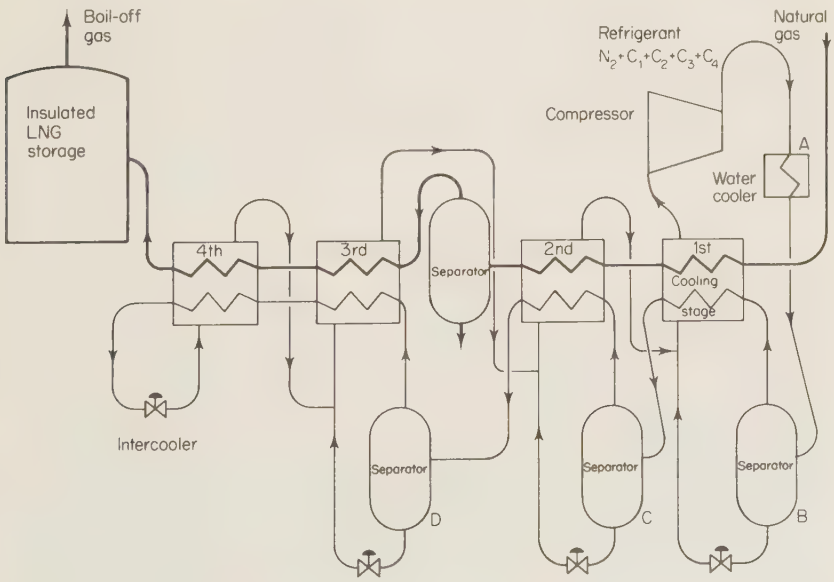

Fig. 3. Simplified diagram of a mixed refrigerant cycle.

and is then water cooled. The higher boiling point components of the refrigerant condense and are separated at point B, then pass into the first cooling stage where they are used to cool both the natural gas and the remaining uncondensed refrigerant at high pressure, by vaporizing. The refrigeration process is controlled so that a liquid is condensed at point C, which will be a suitable refrigerant for the next stage where the natural gas and the uncondensed high-pressure refrigerant will be further cooled. This process can be repeated as often as necessary, so that ultimately liquid methane is subcooled so that it can be stored in a low-pressure LNG storage vessel.

Storage of LNG

The natural gas liquefied down to low pressure by the means described above now needs to be stored. There are a number of different systems, but all assume that the LNG will be kept cool, i.e. the pressure will stay low. However, there will inevitably be a degree of boil-off as a result of heat transfer from the outside ambient air. The boil-off gas may be used in the liquefaction process or alternatively be recompressed and reliquefied and returned to storage.

Storage vessels may be either above ground, double-wall, high-nickel steel vessels with a high-quality insulation material between the walls, to the more expensive but less obtrusive, frozen-earth, underground storage. A third method is to use prestressed concrete backed up with a perlite insulation; these storage tanks can be designed to be both under and above ground to suit the site conditions and local safety requirements and regulations.

Evaporators

The final stage before use for the LNG is to revaporize the methane to gas that can be piped to the point of consumption. Obviously these vaporizers need to be made of materials capable of standing the sort of temperatures and pressures of an LNG feed. The heat source will be something cheap and available, and often the most readily available substance is sea water. This will either be used indirectly or its heat will be transferred to another appropriate fluid, e.g. liquid propane.

Uses

The uses of a gaseous fuel are wide and various, and these will be dealt with at length, together with the uses of LPG.

Liquefied Petroleum Gas

This term refers to mixtures of C_3 and C_4 hydrocarbons which are predominantly propane, propylene, n-butane, butylene, and iso-butane. Table VII indicates that whereas methane (CH_4) and ethane (C_2H_6) are permanent gases, i.e. normally above their critical temperatures, propane (C_3H_8) and higher hydrocarbons will liquefy under pressure at normal ambient temperatures. For this reason they are a valuable hydrocarbon fuel, since they

TABLE VIII
Properties of Commercial Propane and Butane

	Propane	Butane
Relative density of liquid at 15°C (60°F)	0.50 to 0.51	0.57 to 0.58
Imperial gallons/ton at 60°F	439 to 448	385 to 393
Litres/tonne at 15°C	1 965 to 2 019	1 723 to 1 760
Relative density of gas compared with air at 15°C (60°F) and 1 016 mbar (30 in Hg)	1.40 to 1.55	1.90 to 2.10
Volume of gas (ft^3) per lb of liquid at 60°C and 30 in Hg	8.6 to 8.7	6.5 to 6.9
Volume of gas (litres) per kg of liquid at 15°C and 1 016 mbar	537 to 543	406 to 431
Ratio of gas volume to liquid volume at 15°C (60°F) and 1 016 mbar (30 in Hg)	274	233
Boiling point at atmospheric pressure		
°C (approx.)	−45	−2
°F (approx.)	−49	28
Latent heat of vaporization (Btu/lb) at 60°F	154	160
Latent heat of vaporization (kJ/kg) at 15°C	358	372
Specific heat of liquid at 60°F (Btu/lb°F)	0.60	0.57
Specific heat of liquid at 15°C (kJ/kg°C)	2.512	2.386
Sulphur content, % weight	Negligible to 0.02	Negligible to 0.02
Limits of flammability (percentage of volume of gas in a gas air|mixture to form a combustible mixture)	Upper 10.0 Lower 2.4	Upper 9.0 Lower 1.9
Calorific values		
Gross (Btu/sft^3 dry)	2 500	3 270
(MJ/sm^3 dry)	93.1	121.8
(Btu/lb)	21 500	21 200
(MJ/kg)	50.0	49.3
Net (Btu/sft^3 dry)	2 310	3 030
(MJ/sm^3 dry)	86.1	112.9
(Btu/lb)	19 900	19 700
(MJ/kg)	46.3	45.8
Therms/ton (gross CV)	482	475
GJ/tonne	50.0	49.3
Air required for combustion		
(ft^3 to burn 1 ft^3 of gas at STP)	24	30
(m^3 to burn 1 m^3 of gas at STP)	24	30

can be stored as a liquid with a high thermal density, but used as a gas with all the attendant advantages.

The sources of LPG are the same as the sources of natural gas as already described. Even after stabilization of the crude, however, some C_3 and C_4 hydrocarbons remain in solution which are recovered during the subsequent distillation. In addition, during various other refinery processes such as catalytic reforming, thermal cracking and reforming, further LPG is released.

The yield of C_3 and C_4 hydrocarbons varies very considerably from one crude source to another, particularly for associated and unassociated gases, as can be readily seen from Table I. That derived from the crude oil after stabilization is usually of the order of 2 per cent to 4 per cent of the barrel.

As already described, natural gas (methane) is ultimately distributed to users by pipeline. LPG on the other hand can be readily transported as a liquid by

FIG. 4. LPG road tanker. (Courtesy of BP Oil Ltd).

means similar to other liquid fuels. Thus the most usual method is by road tanker (up to 17 tonnes of product) or rail tank wagon (from 20 tonnes to 100 tonnes per wagon). Figure 4 shows a typical 15 tonne capacity road tanker, and Fig. 5 is a block train being discharged at an industrial plant. In order to maintain the product in its liquid state, however, it has to be kept under pressure and the tanks are therefore pressure vessels. This pressure must be maintained during all activities, from storage at the refinery, to transfer into the road tanker, or rail tank wagon, and then in the storage vessel at the users' premises.

In addition to the modes of distribution described above, there is also the transportable container which is now a familiar feature in all kinds of activity. These vary from tiny disposable cartridges of less than 100 g, to the larger refillable steel or aluminium alloy cylinders ranging up to around 50 kg of product. These are filled at purpose-designed filling plants and distributed by road or rail transport to the retail outlet.

At the other end of the scale there is also the transport and storage of LPG in a refrigerated state. Large international sea transport cargoes are usually refrigerated, whilst refrigerated land storage is only economically justified for storage measured in thousands of tonnes and for import/export terminals, Fig. 6.

Thus, most inland transport and storage is as a liquid at ambient temperature under pressure. The pressure is simply created by the natural vapour pressure of the product which varies with its temperature. Butane has a lower vapour pressure than propane. The carrying vessels, whether they are road tankers, static storage, cylinders or cartridges, must be designed to accept

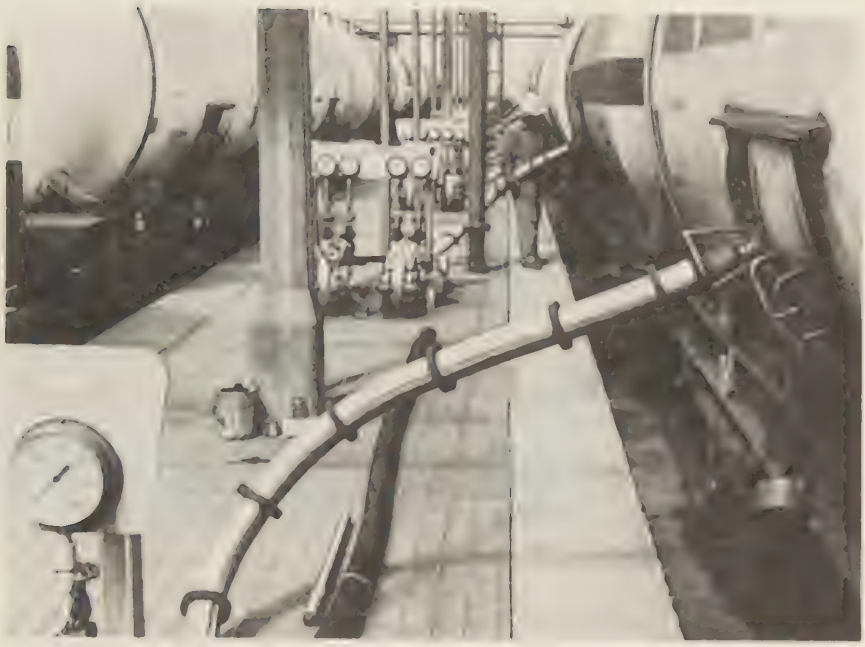

FIG. 5. Block-train delivery of butane to an industrial customer.

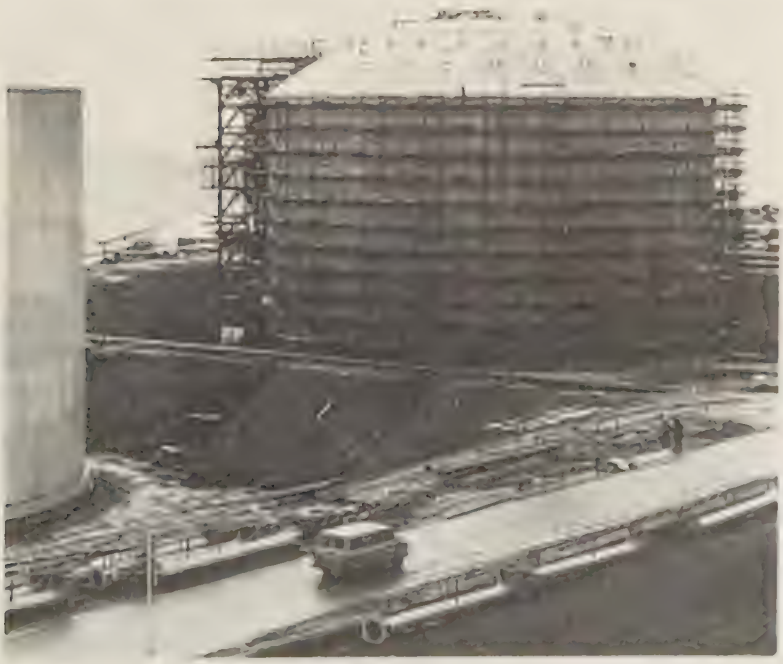

FIG. 6. Refrigerated LPG storage under construction at Sullom Voe. (Courtesy of BP Oil Ltd).

the highest pressure likely to occur in service. A knowledge of the highest ambient temperature, and the grade of product is thus essential.

There are usually nationally accepted standards for commercially available LPG. In the UK, for instance, commercial propane and commercial butane are marketed as separate grades conforming to BS 4250. In some other countries mixtures of propane and butane are marketed. The climate is usually the governing factor. The maximum vapour pressure of commercial propane and commercial butane to BS 4250 for various temperatures is illustrated by the graph (Fig. 7).

Storage vessels for LPG range from those for major industrial users and refineries of 1000 tonnes capacity or more, down to small industrial or commercial users of 1 tonne or less. Even smaller vessels down to 500 litres designed for on-site refilling are available for domestic purposes, i.e. heating and cooking. Similar vessels are sometimes used for permanent caravan sites, and holiday homes. Figures 8 and 9 illustrate a large and small storage installation for industrial use.

Deliveries to these installations are usually by road tanker. The tanker

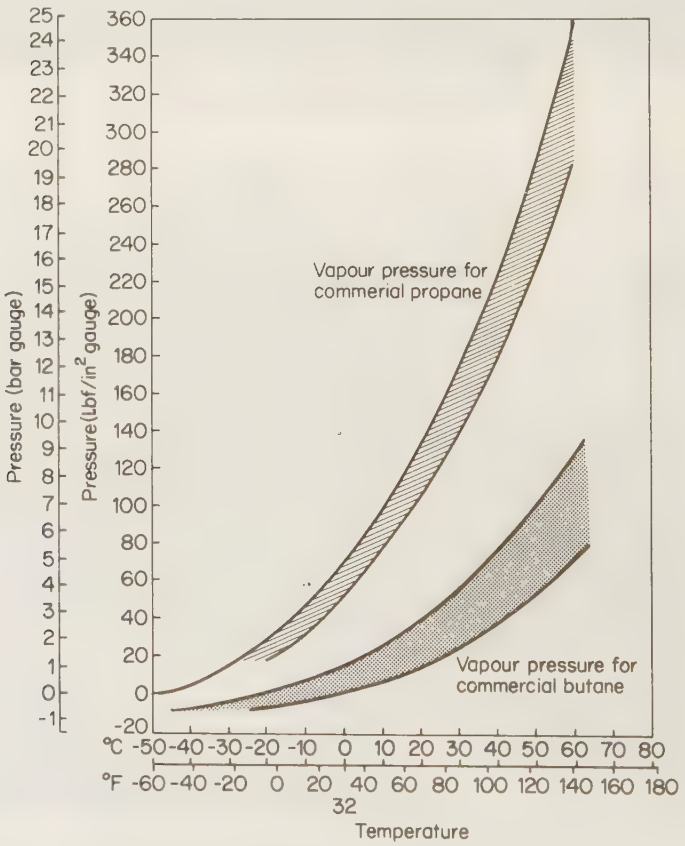
Pressure (bar gauge)
Pressure(Lbf/in² gauge)
Vapour pressure for commerial propane
Vapour pressure for commercial butane
°C -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80
°F -60 -40 -20 0 20 40 60 80 100 120 140 160 180
32
Temperature

FIG. 7. Vapour pressure/temperature curves for LPG.

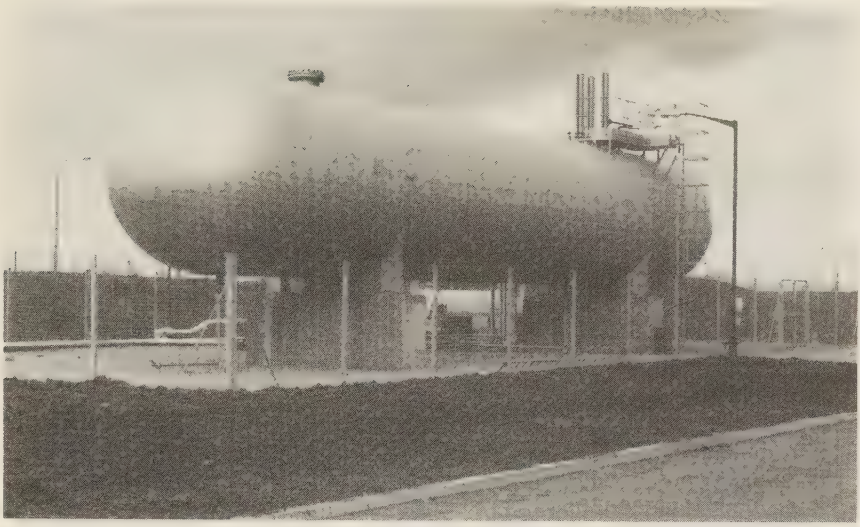

FIG. 8. Typical large industrial butane storage installation.

carries its own off-loading pump driven by the vehicle engine, and the transfer is by a flexible hose which is connected to the receiving vessel by a gas-tight coupling.

It is apparent from the vapour pressure curves that to obtain a gas supply from a storage vessel, or from a cylinder, it is only necessary to release it from the top vapour space. Propane can be supplied from storage to the plant without any pumps or compressors.

Butane in cylinders used for domestic purposes is also used in this way. However, in the case of bulk storage of butane for industrial and commercial purposes, the vapour pressure is generally too low to use this simple method and

FIG. 9. Small industrial propane storage installation. (Courtesy of BP Oil Ltd).

FIG. 10. Direct fired butane vaporizers.

use is made of a liquid feed from the bottom of the storage vessel via a pump, to a vaporizer. The vaporizer is simply a heat exchanger using hot water, steam, electricity, and even direct flame as the source of heat. Figure 10 shows a bank of direct-fired vaporisers.

A glance at the vapour pressure curve for butane will, however, reveal that in winter there is a possibility of butane vapour liquefying after the vaporizer if the temperature is allowed to fall in the pipeline even at moderate pressure. For this reason such pipework is usually heated, either by electrical tapes, or if available by steam or hot-water lines.

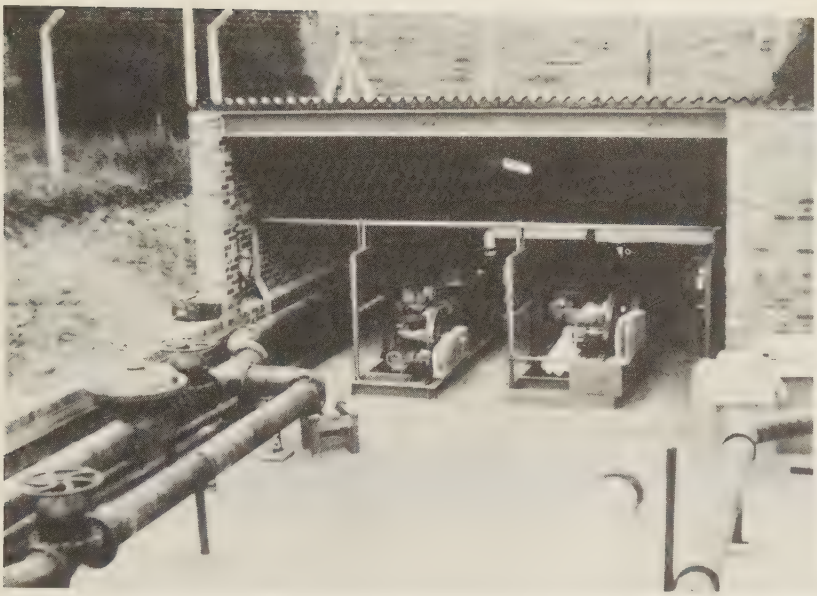

FIG. 11. LPG–Air mixing plant at an industrial plant.

There is an alternative to using neat butane vapour, however, which overcomes the need for pipework heating. This is to use a gas–air mixture. A special gas–air mixer is used which ensures that a preset ratio is maintained at all demand rates. The ratio chosen must be well outside the flammable limits. A typical LPG air mixing plant is illustrated by Fig. 11.

The effect of the air is to depress the vapour dew-point temperature. A further advantage is that the physical properties of the gas can be made to 'simulate' another gas, e.g. natural gas, or manufactured town gas. Such a simulated gas will produce the same heat release through a burner if the supply pressure is the same. It is characterized in the UK by a term known as the wobbe number.

$$W = \frac{\text{Calorific value}}{\sqrt{\text{Specific gravity of the gas (Air} = 1)}}$$

The gas–air ratio is therefore chosen to achieve the desired wobbe number. However, the use of a simulated gas for plant conversion may not entirely avoid burner adjustment or modification, if other properties differ markedly, e.g. flame speed.

The supply of propane or butane from storage or vaporizer to plant is usually governed down to a medium pressure of around 1.5 bar, for final reduction to between 28 and 37 mbar at the burner. However, the versatility of LPG is such that plant and combustion equipment designers can for specialized purposes select virtually whatever pressures are most suitable for their requirements.

An unusual but successful alternative system has been applied for some very large high energy consuming plants. This involves using liquid-phase LPG right up to the burner.[1]

The storage and handling of LPG requires considerable attention to safety by all concerned with it. Most countries have codes of safe practice recognized by industry, or in some cases enforced by law. The Institute of Petroleum Code No. 9[2] often forms the basis for national requirements. Typical properties of commercial LPG are shown in Table VIII.

Uses of Gaseous Fuels

Gaseous fuels derived from petroleum sources, i.e. natural gas and LPG, have many advantages over the alternative liquid fuels, and are regarded as 'premium fuels'. Some of the premium characteristics are:

Very low sulphur
Easy ignition
Simplicity of burner design
Versatility—e.g. very small flames, localized heating
Wide turn-down of burners
Clean combustion gases
Ease of control

The spread of gas for domestic central heating is well known, but it has also found many industrial applications, particularly where the premium characteristics of the fuel can show an overall financial benefit against alternative fuels or energy sources.

The versatility of gaseous fuels has resulted in a great variety of sometimes quite ingenious burners, particularly at the small output end. Even at the modest pressures of natural gas supplies, the ability to induce its own primary air supply has resulted in a range of atmospheric burners (Fig. 12). Because of the small flames possible, bar and ribbon burners of this type are available which can spread the heating over a long distance (Fig. 13). They can also be designed into various configurations to suit special heating requirements. The familiar domestic gas ring works on this principle. Another common application of atmospheric burners is for immersion tube firing for tank heating.

Higher heating rates and higher temperatures are usually achieved by

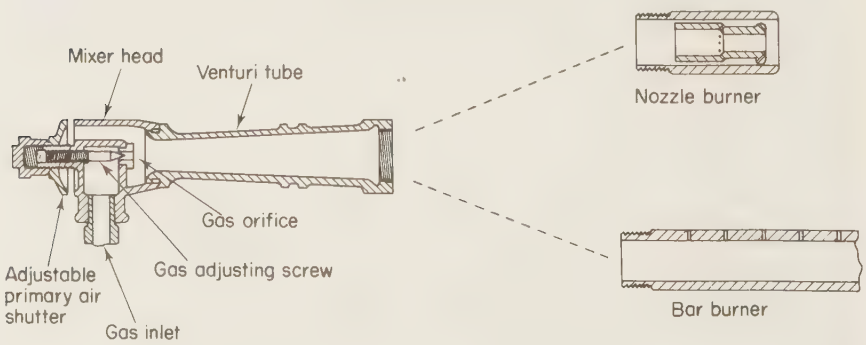

Fig. 12. Section of a typical atmospheric gas burner.

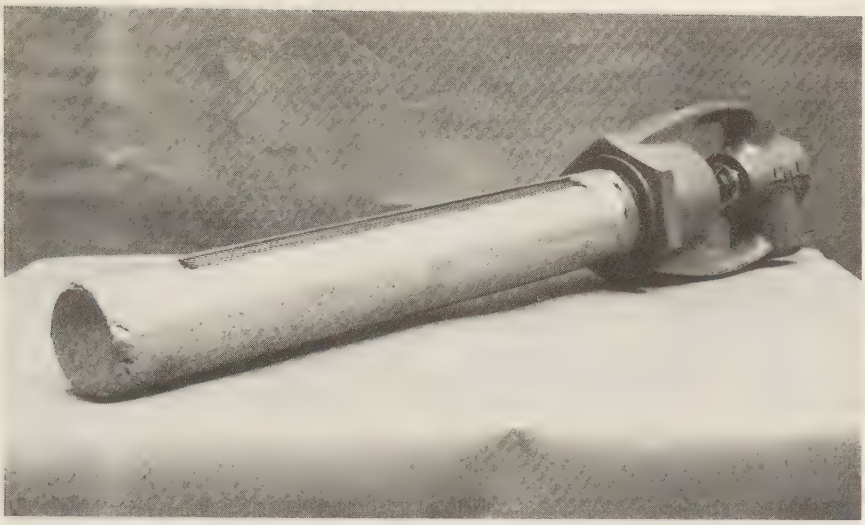

FIG. 13. Industrial ribbon burner. (Courtesy of Acrogen Ltd).

premix burners using an air fan and mixing device to achieve high combustion intensities. They are particularly useful for high-temperature furnace work.

Nozzle-mix burners have some advantage over premix and atmospheric burners. They eliminate the possibility of flash-back, and have a very wide turn-down capability. They can operate with complete stability from an excess gas condition, to an excess air condition of several hundred per cent where required. This type of burner is the most usual for boiler applications, but also finds many other uses.

The concentration of heat into a localized area is a very useful feature which has been developed into a 'rapid heating' technique using special high-intensity tunnel burners and a high-pressure air supply. The high velocity combustion gases impinge upon the work piece, raising the heat transfer rate many times over conventional furnaces. Gas-fired rapid heating machines have been developed for a wide range of applications such as billet heating (Fig. 14), and sheet metal heat treatment. A similar but older technique of concentrating a tiny but very high temperature open flame, or array of such flames, has been used for the making of electric light bulbs for many years. The very specialized machines use pure oxygen instead of air to attain the very hot flames that permit fast production.

Another ingenious use of the versatility of gaseous fuels is the radiant panel. Used primarily for space heating it relies upon combustion with air taking place inside tiny ports or even the pores of a ceramic plaque which glows red hot.

The clean combustion which can be achieved with gas is such that direct make-up air heaters are available for industrial use in such buildings as warehouses where heat losses are high due to the rate of ventilation. The hot combustion gases are diluted with air to bring down the temperature to an acceptable level and to ensure that combustion product levels are within acceptable limits, and then discharged directly into the work place. There are

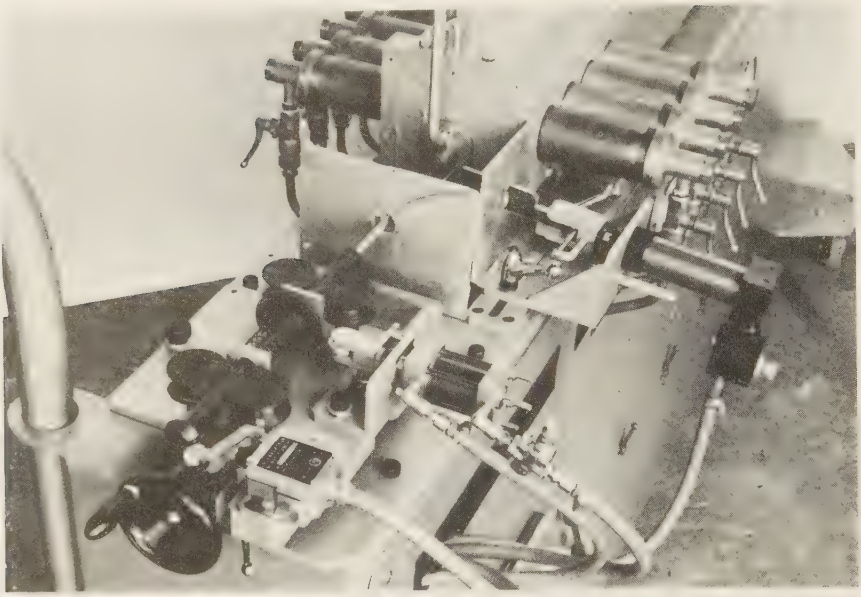

FIG. 14. Rapid heating machine for brass billets. (Courtesy of Shell UK Oil Ltd).

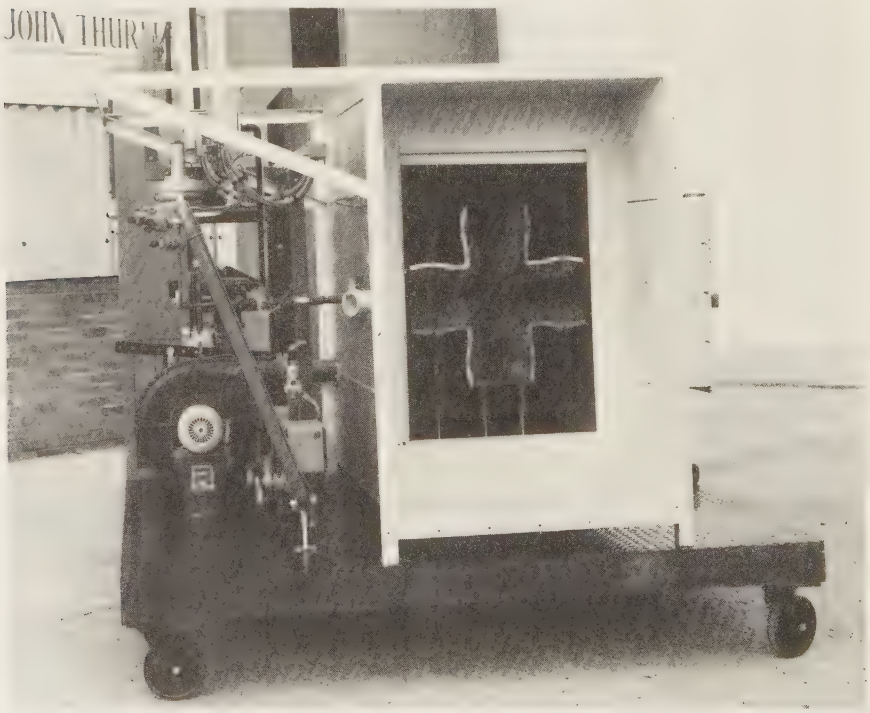

FIG. 15. Direct make-up air heater. (Maxon) (Courtesy of John Thurley Ltd).

FIG. 16. Top-fired continuous brick kiln converted from coal to gas firing.

then no flue losses, which ensures a high thermal efficiency. Figure 15 shows a typical unit.

Gas has long been established in the firing of pottery and fine ceramics, but it has now been established in the heavy clay industry in the UK. This has largely been at the expense of hand-firing with coal. The dramatic improvement in firing times more than offsets the difference in thermal cost of fuel. Figure 16 shows a continuous kiln being top-fired with butane.

An interesting development in the use of butane was established for firing certain types of lime kiln, and also for aggregate driers. Instead of using the fuel as a gas, it was retained in the liquid phase right to the burner by maintaining

FIG. 17. Lime kiln fired with liquid phase butane. (Courtesy of Amey Roadstone Corp. Ltd).

adequate pressure and then treated as a liquid fuel.[1] This eliminates the use of vaporizers, and pipeline heating, and considerably reduces pipe sizes. However, the high pressure of the system involves a very high standard of installation, and the economics as compared to a more conventional system need to be assessed in each case. A very large shaft/rotary lime kiln which is fired on liquid phase butane is shown by Fig. 17.

Gaseous fuels have been used as engine fuels from the earliest times. For stationary purposes some of the earliest internal combustion engines were gas engines. There are now a wide range of spark-ignition engines designed for natural gas, and LPG. Gas has also been used as an automotive fuel, but from a practical point of view only LPG offers a solution to the low energy density of gaseous fuels. Natural gas can of course be compressed, but the fuel tank would

FIG. 18. Automotive LPG filling station.

then be very heavy to accommodate pressures of the order of 200 bar or around 3000 lb/in^2. LPG on the other hand, as already explained, can be carried liquefied under relatively low pressure, and provides an energy density more similar to petrol.

Filling LPG vehicle tanks is relatively simple and some self-service installations are in operation. A gas-tight self-sealing coupling is necessary of course, and a typical trigger operated design is shown in the photograph, Fig. 18. The avoidance of overfilling the tank is essential, the usual limit being

80% of the volume. The maximum fill level is either controlled automatically by a float cut-off device, or by the operator observing the tiny bleed from a fix dip tube which can be opened during filling. The filling is stopped as soon as the bleed indicates liquid. This is a very reliable method. Any automatic device needs to have a similar high reliability. To avoid overstressing the tank from whatever cause, including inadvertent overfilling, all tanks have a pressure relief valve.

The viability of automotive LPG, normally commercial propane, or in some countries a mixture of propane and butane, depends very considerably upon national taxation policies. Many countries favour LPG with beneficial tax over petrol, and that together with the basic pricing policy of the suppliers can give an economic advantage to LPG, but this has to be weighed against the cost of conversion. At the time of writing few motor vehicles are produced for running on LPG as original design. Most are converted to dual fuel running after delivery. Few countries have an extensive network of LPG refilling stations and the dual fuel arrangement provides the insurance against running out of LPG. Filling up with LPG has no problems, as shown by Fig. 18.

The advantages of LPG-fuelled motor vehicles is greatest for the fleet owner, particularly if he can install his own bulk storage and dispensing equipment. This is the sector of this market most likely to continue expanding.

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Aviation Fuels

By R. A. VERE

INTRODUCTION

Since the beginning of powered flight the energy supplying the power has been obtained from hydrocarbon fuels. Although the tremendous advances in rockets, used for launching space satellites, has brought a new concept to energy sources, aviation fuels derived from crude oil will continue to supply the propulsion energy for conventional aircraft for many years to come. Since the 1973 oil crisis there has been a realization that crude oil will not last for ever and conservation measures have been introduced. Recently several studies have been carried out seeking to make jet fuel, the major fuel for aircraft, available in greater volumes from the same volume of crude oil to meet the changing demand pattern from a barrel of crude oil.

The 1950s saw the commencement of a huge expansion in civil commercial aircraft fleets with the turbo-prop replacing the gasoline-powered piston engine. The 1960s saw a change again, this time the major airlines converted to the much faster pure jet and the early 1970s saw the introduction of the wide-bodied commercial aircraft, starting with the Boeing B-747 known as the 'jumbo-jet'. As we get into the 1980s the overriding problems are fuel cost and availability. Tremendous strides are being made in the aircraft industry to produce fuel efficient aircraft by improved engine efficiency and by reducing drag on the aircraft.

The main demand for aviation fuel is for aviation turbine fuel; there is a continuing decline in the volume of aviation gasoline. Aviation gasoline use is now largely confined to General Aviation, a term which embraces small light aircraft used by private companies, air taxis and, of course, the private flier. Although the number of aircraft in this sector is growing the aviation gasoline volume, as a percentage of total aviation fuel consumed, is steadily decreasing.

AVIATION GASOLINE

Aviation gasolines for use in aircraft spark-ignition piston engines have been in use for more than fifty years. The incentive for more power from less weight with a low fuel consumption and for considerable operational flexibility, spurred on considerably by two world wars, military aircraft playing a very significant part in World War II, supported continuous research and development on aviation gasolines. Owing, in no small way, to the close relationship between the aircraft industry, operators and fuel suppliers, there was a considerable advance in fuel quality and production processes until 1945.

Since that time the aircraft industry has swung from the gasoline-fuelled piston-engined aircraft to the 'wide-cut' and kerosine-fuelled gas turbine engine. Today no new aircraft of any size are being built using piston engines,

TABLE I

Aviation Gasoline Specification DERD 2485

Property		Limits		
		Grade 100 LL	Grade 100	Grade 115
Appearance		Clear, bright and free from solid matter and undissolved water at normal ambient temperature		
Aromatics, % vol	min	—	—	5
Colour, visual		Blue	Green	Purple
Corrosion, copper classification			1	
Density at 15°C kg/l			Report	
Distillation				
Initial boiling point, °C			Report	
Fuel evaporated,				
% vol at 75°C	min		10	
% vol at 75°C	max		40	
% vol at 105°C	min		50	
% vol at 135°C	min		90	
End point, °C	max		170	
Sum of 10% and 50% fuel evaporated temperatures	min		135	
Residue, % vol	max		1.5	
Loss, % vol	max		1.5	
Existent gum, mg/100 ml	max		3	
Freezing point °C	max		−60	
Knock rating, Lean mixture				
Motor method: Octane number	min	99.5	99.5	—
Performance number	min	—	—	115
Knock rating, Rich mixture				
Performance number	min	130	130	145
Oxidation stability, 16 hour				
Potential gum, mg/100 ml	max		6	
Precipitate, mg/100 ml	max		2	
Reid vapour pressure at 37.8°C, kPa	min		38.0	
	max		48.5	
Specific energy, net J/g	min	43 500	43 500	44 000
or				
Aniline gravity product	min	7 500	7 500	9 800
Sulphur, total, % mass	max		0.05	
Tetraethyl lead content as g Pb/l	max	0.56	0.85	1.28
Water reaction				
Interface rating	max		2	
Separation rating	max		2	
Volume change, ml	max		2	

although some are still in use. However, there is an increasingly flourishing market for light aircraft using piston engines requiring gasoline, but these aircraft are designed for the lower quality of aviation gasoline.

Although no research and development of gasolines has been carried out since 1945 it is still of interest, and for this reason the development of aviation gasoline is presented.

Aviation Gasoline Specifications

The essential function of any specification is to ensure suitability and subsequently uniformity of product; this is especially true of aviation fuels where consecutive refuellings are separated by hundreds if not thousands of miles. The current aviation gasoline fuel specifications are the result of co-operation between fuel suppliers, engine manufacturers, and various government departments.

Table I lists the chemical and physical requirements for aviation gasolines as laid down in the British Ministry of Defence specification DERD 2485. In the United States there are an equivalent military specification MIL-G-5572F and a civil ASTM specification D-910. These three specifications are accepted as the standards of fuel quality by the aviation industry's engine builders for aviation gasoline today. The earliest specifications for aviation gasoline go back over fifty years, the first British specification being issued in 1930 and designated DTD 134.

Aviation Gasoline Grades

There are now only a few airlines still using piston engines. These tend to be the small airlines operating a freight service. The last such aircraft to use London Heathrow was in September 1981. This was a DC-6B from a Helsinki cargo carrier and was its last commercial flight after 24 years' operation. The main users of aviation gasoline are the general aviation aircraft, air-taxis, flying schools, agricultural aircraft, and private fliers. Although their numbers are quite large the volume of fuel consumed is small. Due to this change the number of aviation gasolines grades has been reduced. DERD 2485 covers three grades: Avgas 100LL, Avgas 100, and Avgas 115/145. The USA military MIL-G-5572 F covers three grades called 80/87, 100/130 and 115/145, and the United States civil specification ASTM D-910 lists three grades—80, 100, and 100 LL.

The grade nomenclature gives the anti-knock quality of the fuel by the two defined methods. Where only one rating is quoted in the grade, e.g. Avgas 100, the second anti-knock quality is still a requirement of the fuel. Anti-knock quality defined by the first number is the lean-mixture rating determined by the joint method ASTM D 2700/IP 236, and that defined by the second number the supercharge rating by either ASTM D-909 or IP 119. The numbers refer to octane numbers up to 100 and Performance Numbers for ratings above 100.

In the past there has been five different quality levels of aviation gasoline. In the UK these were classified as follows:

Grade 73	Non-leaded aviation gasoline for light aircraft.
Grade 80	An aviation gasoline for light aircraft containing a maximum TEL content of 0.5 ml/US gal. In the UK to meet the DERD 2485 specification this grade had to be without TEL, i.e. lead-free.
Grade 91/96	A leaded gasoline containing up to 20 per cent of catalytic light ends for use in medium-powered aircraft.
Grade 100/130	A leaded blended gasoline for use in medium-range transports and military aircraft.
Grade 115/145	A leaded high-performance blended gasoline for long-range transport and high-powered military aircraft.

Due to low volume usage the grades 73 and 96 have been withdrawn. In the early 1970s grades 80 and 100/130 were withdrawn and replaced by one product known as 100 LL. The LL stands for low lead and is so-called because the grade 100 LL has exactly the same properties as the grade 100/130, but whereas grade 100/130 has a maximum lead addition of 4.60 ml/US gal the 100 LL grade has a maximum lead level of 2.0 ml/US gal. This was done to reduce the impact of the lead level increase on engines designed for grade 80 at 0.5 ml/US gal maximum lead.

Soon after the introduction of the one 100 LL grade there was a spate of problems from light aircraft due to spark-plug fouling, and high cylinder-head temperatures leading to cracked cylinder heads. As a result of much discussion, including a two-day symposium in Stockholm in 1976, the old grade 80 has been reintroduced on a limited scale in the USA and some European countries.

Aviation gasolines are colour-coded for identification purposes. The grade colours are as follows:

Grade	*Colour*
80/87	Red
100 LL	Blue
100/130	Green
115/145	Purple

AVIATION GASOLINE QUALITY REQUIREMENTS

Anti-knock Properties

'Knock' in a piston engine is the principal limiting factor to the possible power output obtainable from it. Any reciprocating gasoline engine can be made to operate under knock conditions if run on an unsuitable gasoline grade; i.e. one possessing less than the desirable minimum anti-knock properties for the selected running condition. This phenomenon of knocking manifests itself as a sharp metallic hammering in the engine cylinder.

Ideally, a flame, initiated by the ignition of the air/vapour mixture, progresses smoothly and steadily from the spark plug zone throughout the vapour space to its farthest extremities. That portion of the charge situated ahead of the flame front is progressively heated by radiation and conduction from the expanding flame itself and also by compression due to the expanding burning products.

A condition can be reached where the temperature of the unburnt gases is sufficient to cause their self-ignition before the arrival of the flame front. This results in an extremely rapid pressure rise the peak of which is slightly ahead of the normal operating pressure peak, leading to a loss of power and eventual overheating. Should this knock condition occur occasionally in a motor-car engine it would be termed no more than a nuisance. However, in a piston-engined aircraft the general noise level is so high that fuel knock could readily persist undetected. In this circumstance, overheating will rapidly occur and be further aggravated by the onset of pre-ignition from carbon deposits, overheated plugs, and exhaust valves. The combination of intense pressure

waves and overheating can be most destructive, and leads to piston failure in a few minutes.

Clearly, it is most necessary that conditions conducive to fuel knock shall be limited in any engine in service. The tendency towards fuel knock is increased by any factor which causes:

(a) A decrease in the main flame velocity in the combustion chamber;
(b) A shorter period for ignition of the unburnt gases beyond the flame front.

In practice it is found that many such engine factors exist, and the requirements for avoidance of knock are not therefore vested in the fuel alone. For example, compression ratio, degree of supercharge, shape of combustion chamber, positioning of valve ports and spark plugs, oil consumption and general cleanliness of the combustion zone, temperature and pressure of the charge, mixture strength, turbulence within the cylinder, ignition timing, and type of spark plug can all vary the tendency to knock. It is therefore vital that the installed engine and the operating conditions permissible shall be contrived to avoid knock when using a gasoline of known minimum anti-knock properties.

The most important practical consideration for the engine designer is the limitation of compression ratio for operation on any given fuel grade, and hence of thermal efficiency, performance, and economy. It was the quest (and primarily military need) for improvements in these engine characteristics which led to the production and marketing of fuels of known high anti-knock properties. There remained the problem of defining and measuring anti-knock quality.

In fact special engines were required, and the ones now generally accepted for knock-rating determinations are based on the single-cylinder variable compression CFR engine. However, it was also necessary to establish arbitrary scales of fuel anti-knock performance, since knock cannot be measured in absolute units.

Anti-knock rating scales

Octane number scale. The octane number is defined as the volume percentage of iso-octane (2,2,4-trimethyl pentane) in a blend with n-heptane which is equal to the test fuel in knock intensity under the standardized and closely controlled conditions of test in the CFR engine. Thus, a fuel of 90 octane number has a CFR engine performance matching that obtainable with a blend of 90 per cent volume iso-octane (of good anti-knock properties) and 10 per cent volume n-heptane (of poor anti-knock properties). These compounds were chosen arbitrarily and assigned values of 100 and 0, respectively, on the octane scale. They are both pure hydrocarbons and thus their quality can be adequately controlled. Standardization fuels have also been evolved for use in CFR engine checks consisting of blends of suitably sensitive aromatics, n-heptane and tetraethyl lead (TEL). These blends are not used for fuel ratings, but for the regular checking of the engine and operating conditions.

TEL is a mixture of tetraethyl lead $(C_2H_5)_4Pb$ and ethylene dibromide,

together with an identifying dye and kerosine; it is capable of improving the anti-knock rating of fuel when added in very low concentration and is discussed in some detail later.

Performance number scale

Fuels with anti-knock ratings better than that of iso-octane clearly cannot be rated on the normal Octane Number scale. Addition of TEL to iso-octane greatly improves its anti-knock properties, and fuels of higher than 100 ON are matched in knocking characteristics against iso-octane/TEL blends. The measured results so obtained are converted into Performance Numbers (PN) by which fuels of more than 100 ON are designated in specifications.

The Performance Number scale is based on engine power output, and was evolved to permit a clearer understanding of anti-knock values than is possible using the heptane/octane or octane/TEL scales. It was derived empirically from a survey of the knock-limiting power obtainable from many engines using varying amounts of TEL in iso-octane. The PN of an aviation fuel represents approximately the maximum knock-free power output obtainable from an engine using it, and is expressed as a percentage of the maximum knock-free power from that engine using iso-octane under comparable operating conditions. Thus, a 130 PN fuel rating (iso-octane plus 1.25 ml TEL) indicates that approximately 130 per cent of the knock-limited power obtainable from iso-octane at the same mixture ratio can be obtained, provided that the engine is designed to utilize it.

On the PN scale, 100 ON equals 100 PN, and the various blends of iso-octane and TEL are assigned specific Performance Numbers.

Defects in knock rating scales

While considerable progress in the standardization of equipment and procedures has been achieved, some anomalies and defects persist in the scale used.

1. The octane scale is arbitrary and not directly related to engine performance. An improvement of 1 ON at the upper end of the scale is of much more benefit in terms of potential performance than the same improvement lower down. This combined with the fact that the performance and octane scales are related (in fact equal) only at 100 ON, presents difficulties in the calculation of the rating of blends of gasolines with constituents above and below 100, and expensive time-consuming rating tests are necessary.

2. Performance Number is an index of approximate relative engine output in supercharged engine operation only where the manifold pressure is varied to suit the knock value of the fuel, as in IP 119 method.

3. The reference fuels used have quite different temperature sensitivity and mixture response from those of gasolines; hence the results obtained from fuel-rating tests can only serve as a guide for suitability of the test fuel in full-scale engines. For example, iso-octane has a poor rich-mixture rating.

4. A single-cylinder test engine cannot simulate the real conditions in multi-cylinder engines, in particular the effects of mixture strength, TEL, and scavenger distribution in the manifold, and ignition timing and oil

consumption variations between cylinders. Hence these rating tests do not overcome the need for full-scale investigations in a new engine over the full range of control settings to prove the acceptability of a rated fuel (defining weak- and rich-mixture behaviour under highly specialized conditions) for that engine.

The Rich Mixture Method, IP 119, determines the maximum knock-limited power output of a fuel by comparing the knock-limited mixture response curve with that obtained on a standard fuel (Fig. 1). A supercharged version of the CFR engine is used in which the compression ratio is fixed and the test conditions are selected to produce good correlation between CFR engine and full-scale engine behaviour.

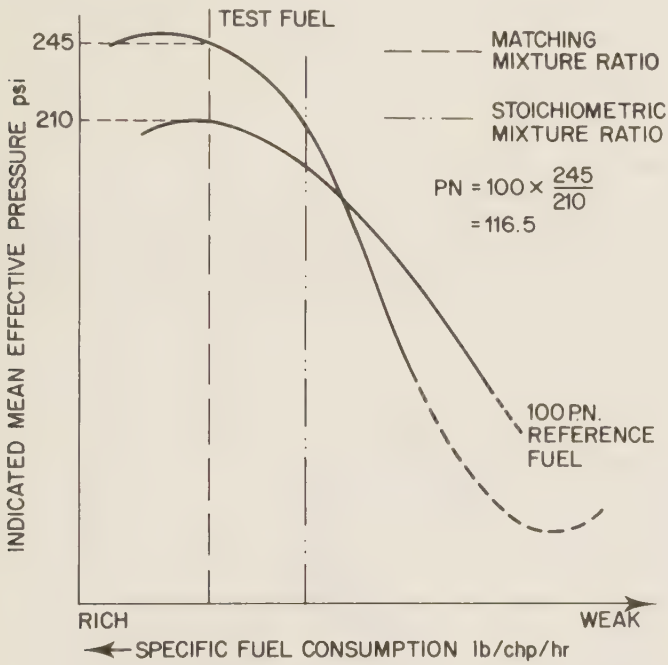

Fig. 1. Rich-mixture rating–mixture response curve.

Essentially the method determines the dependence of the highest permissible power (in terms of indicated mean effective pressure) on mixture strength and boost for a constant light knock condition. The reference fuel blend having the same performance as the test fuel is determined by bracketing. The rating of the test fuel is the directly proportional power relationship between test and reference fuels in terms of imep, at the mixture strength (or equivalent specific fuel consumption) giving peak power with the reference fuel. The reference fuel is heptane/iso-octane up to 100 ON and iso-octane plus TEL above 100 ON. The result is then expressed as an octane number or performance number, respectively. Complete details of the method of tests and engine operating and maintenance standards are contained in the IP and ASTM manuals for rating aviation fuels.

Mixture response

The effect of mixture strength on power for a given fuel is shown typically in Fig. 2. Increments in supercharge give rise to the series of curves (a), (b), (c), and on each of these curves a condition of incipient knock can be established. In Fig. 2 this condition for the power curve (a) occurs at one mixture ratio of 16:1. If all similar knock-limiting points on the curves are connected, a boundary curve, the mixture response curve, can be drawn between knock and knock-free conditions, illustrating that much greater power, by increase in boost, can be employed at rich mixtures. There is, however, a limit to the knock-free power obtainable as shown in curve (c), which represents the maximum boost permissible for take-off. Weakening the mixture from this setting (at constant boost) will move the operating point into knock conditions.

The contact point of the lowest boost curve with the response curve is termed the minimum boost point, for it is under these conditions that the lightly boosted engine is more prone to knock.

Tetraethyl lead and other anti-knock materials

Improvement in fuel anti-knock quality has been shown possible by the addition of very small quantities of TEL. In the early searches for fuel anti-knock improvement many compounds were discovered which had this property in varying degree. Unfortunately, other properties such as inadequate

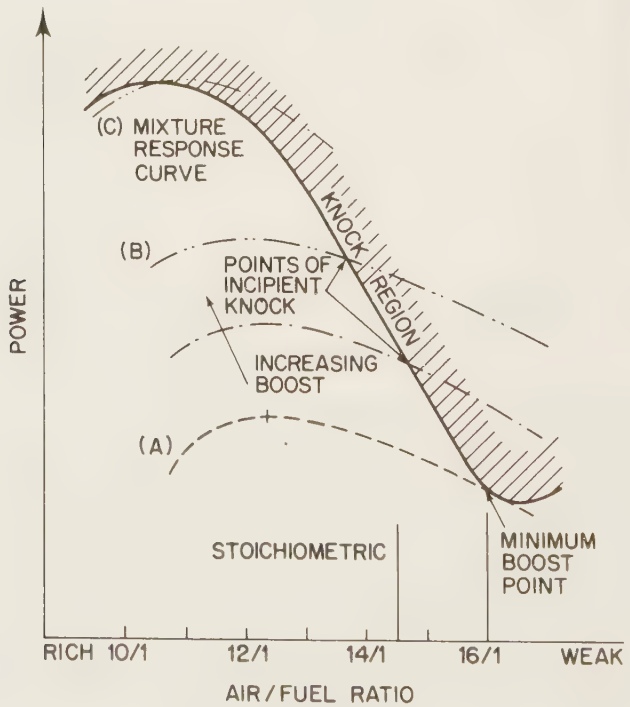

Fig. 2. Mixture response curve.

solubility in the fuel, obnoxious odours in exhaust products, corrosion tendency, and availability were not so satisfactory. Such substances as iodine and iron and nickel carbonyls were in this category where only small concentrations were needed. Larger concentrations of such compounds as benzene, toluene, and methylaniline also gave improvements but, owing to the relatively much greater concentrations needed, were termed blending agents. Of the additives, TEL was by far the most effective and, although toxic in the concentrated form, was found to be acceptable at the levels required in gasoline blends.

The presence of lead oxides from combustion of the TEL would cause fouling of spark plugs and valves, and hot corrosion of exhaust valves and cylinder ports, since lead oxides all possess high melting points and once formed would remain as deposits in the combustion zone. In order to use tetraethyl lead satisfactorily a 'scavenger' or combining chemical is needed to react with the lead oxide to form more volatile lead salts. Such a compound is ethylene dibromide ($C_2H_4Br_2$) (EDB), which produces volatile lead bromide in the cylinder, which can be expelled with the exhaust gases.

A mixture of TEL and EDB scavenger (known as ethyl fluid), containing the theoretical amount of dibromide for complete combination of bromide with the lead oxides formed on combustion is termed a '1-T' mix (one times theoretical). This ratio is always used in aviation gasoline leaded fuels. Excess dibromide cannot be tolerated, for the free bromine formed would be corrosive to engine parts. A dye is added for identification, and the custom is to refer to the concentration of the active TEL anti-knock component in this blend (61.41 per cent TEL and 35.68 per cent EDB by weight with dye and kerosine). Hence, 4 ml TEL/gal would signify an actual ethyl fluid concentration of 6.5 ml/gal. The distribution of TEL and EDB is not uniform between the engine cylinders, and it has become essential to employ special materials for valves, valve seats, plugs, and cylinder heads to minimize attack from leaded fuels. Current blends limit the permissible amounts of TEL for this reason.

It was also found that gasolines respond differently towards the addition of TEL in terms of anti-knock improvement, and increasing amounts of TEL for any one fuel are progressively less effective in improving knock rating. The paraffins generally possess better 'lead response' as it is termed, than (in decreasing order) the naphthenes, olefins, and aromatics. Alcohols have a negative response, while sulphur compounds and lubricating oil (always present in the cylinder) reduce the effectiveness of TEL in all gasolines.

Performance advantages of high anti-knock rated fuels

In any given engine the use of higher anti-knock fuels will not of itself give increased performance. If this improved fuel rating is accomplished by TEL addition, then the lead fouling and corrosion which may ensue would result in doubtful advantage. The performance gain is potential and to realize it the operating conditions must be changed. These changes usually take the form of increased supercharge or increased compression ratio with appropriate modifications in mechanical strength. An increase in compression ratio, with the enhanced thermal efficiency, will improve the operating economy, e.g. the consumption rate will decrease for the same power conditions when using the

higher rating fuel. If more power is required, this is best achieved by an increase in the air/fuel mixture mass flow through the engine, i.e. by increasing supercharge to the higher limit permitted by the improved fuel rating.

In practice both supercharge and compression ratio are usually varied together, for a distinction must be drawn between improvements obtainable in weak- and rich-mixture ratings. Increasing the compression ratio to benefit from a high weak-mixture rating will result in a lowering of the mixture response curve. This in turn will limit the maximum supercharge, unless the rich-mixture rating is also increased by suitable blending or boost fluid is injected for take-off conditions. The rich-mixture rating is more capable of improvement by blending than the weak-mixture rating. Hence the piston aircraft engine has developed to a general pattern of moderate compression ratio and increasing boost pressure.

Volatility

In the combustion process every fuel must be burnt from the vapour state. Hence fuels for the internal combustion engine must be capable of ready conversion from the liquid to the vapour phase within the engine. Engine supply and metering conditions dictate that the fuel shall be liquid up to the point of entry into the manifold and be in the vapour state in the cylinder at the time of sparking. Hence the degree of volatility permitted is very closely controlled. If the volatility were unacceptably low, then difficulties would arise when starting an engine from cold. Liquid fuel entering the cylinders would wash lubricant from piston rings and cylinder walls, and also cause dilution of the crankcase oil. Poor distribution of fuel between the engine cylinders due to only partial fuel evaporation, with some cylinders over-rich and others over-weak, is aggravated in its effect on power and economy when using leaded fuels, because the liquid fuel will carry in it an excess of TEL. The ethylene dibromide scavenger has a lower boiling point than TEL; hence it is delivered with the more volatile fraction of the fuel, resulting in excess of EDB in some cylinders and excess of TEL in others. Thus, the fuel for the complete engine has a decreased anti-knock rating, with corrosion arising from lead in the rich cylinders and from bromine in the weak cylinders.

Should the volatility be too high, the fuel may vaporize in the tanks, particularly at high altitudes, with attendant losses in venting lines and erratic operation of the metering system. A balance, therefore, has to be struck between high and low volatilities. The suitability of a fuel for engine operation with injection and carburettor systems is determined and controlled by means of its distillation characteristics.

The equipment for distillation tests does not attempt to simulate engine fuel evaporation conditions in any way, but the results obtained from it can indicate the ultimate behaviour of the fuel in full-scale engines.

The fuel will have a boiling range since it is a mixture of many hydrocarbons. In practice it has been found that a boiling range from about 30 °C to 150 °C is desirable. A typical distillation curve is shown in Fig. 3, the temperatures at which certain percentages of the fuel distil being plotted. The 10 per cent temperature is indicative of the comparative ease with which an engine can be started from cold, the 40 per cent temperature of the rate for engine warm-up or

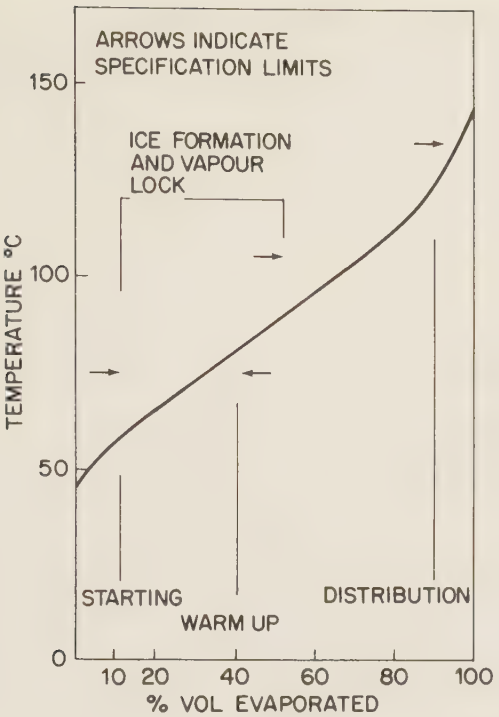

Fig. 3. Typical distillation curve, aviation gasoline, indicating engine performance factors.

stabilizing of slow-running conditions, while the sum of the 10 and 50 per cent temperatures is related to the tendency to form ice in the venturi type carburettor and to vapour locking. The 90 per cent temperature indicates the amount of the less-volatile components present. These are generally not completely vaporized in the manifold, but rely on contact with the hot cylinder and residual exhaust gases for complete evaporation. The lower the 90 per cent temperature, the lower can be the minimum charge temperature encountered in flight at which the fuel will be well distributed and evaporated prior to sparking. The final boiling point of the fuel is specified to avoid the inclusion of hydrocarbons with excessively poor volatility.

Vapour pressure and vapour evolution

A liquid will boil when its vapour pressure is equal to or greater than that of the atmosphere on its surface. A gasoline mixture will therefore commence to boil in a fuel tank when the atmospheric pressure acting upon it (and decreasing with altitude) falls to that of the vapour pressure of the fuel at the prevailing temperature. Dissolved air is also present in the fuel; this too will commence to be released from solution immediately the pressure above the fuel is decreased. However, the volume of air is small in relation to that of fuel vapour.

The standard distillation test does not measure accurately the initial volatility of a gasoline. The 10 per cent evaporated point, specified as a maximum

temperature, is inadequate for determining the very volatile components or the quantity of dissolved petroleum gases present. These constituents are the first to come out of solution with decreasing surface pressure. The effects of their evolution are to cause loss of fuel from the tank vents at altitude, with consequent decrease in range or performance, and the entrainment of released vapours in the engine supply lines unless special design precautions are taken to prevent it.

The increased rates of climb and operational altitudes of modern transport aircraft have necessitated the use of boost pumps fitted with deaerator cones to reject vapour back to the tanks, together with careful design and lay-out of the feed lines from tank to engine to avoid high local temperatures and undue pressure losses in them. (A mixture of vapour and liquid fuel cannot be readily pumped or accurately metered and can lead to complete cessation of flow in feed lines.)

Short of pressurizing the fuel tanks (with the added complications and weight penalties) little can be done mechanically to prevent fuel losses due to boiling. Suitable refining treatments and blending formulations can, however, control the quantity of highly volatile constituents in the fuel to prevent excessive vapour pressure. The test used to measure the vapour evolution characteristics is known as the Reid vapour pressure test. It gives a result lower than true vapour pressure, but is generally within 4 per cent. Practically all aviation gasolines are limited to between 38 and 48.5 kPa at 37.8°C (5.5 and 7.0 psi RVP at 100°F), the lower limit being included to control volatility requirements for starting and to control the atmosphere above the fuel space in the tank. The upper limit is that found generally acceptable for prolonged high-altitude flight without excessive vent loss.

The curves of Fig. 4 illustrate the extent of vapour evolution at altitude for a

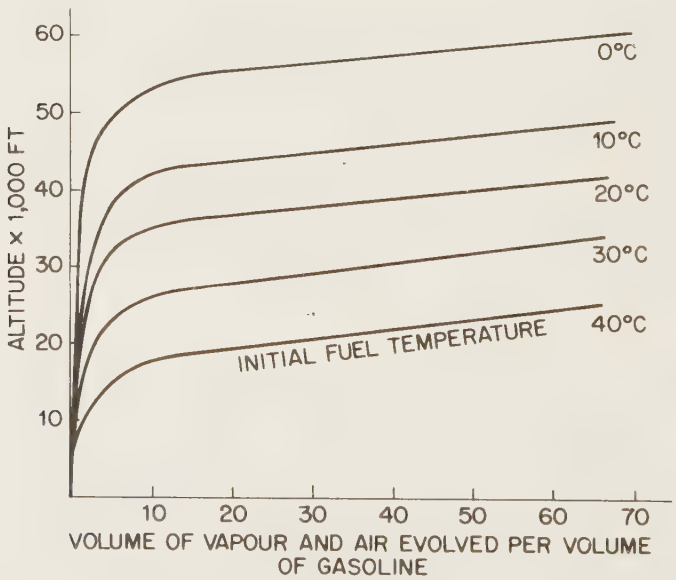

Fig. 4. Typical vapour evolution from aviation gasoline.

range of fuel temperatures recorded at take-off. The higher the initial fuel temperature (such as tropical take-off conditions) the lower the altitude at which fuel boiling will occur. Assuming the fuel to follow the atmospheric temperature/altitude relationship (standard ICAO variations as depicted in Fig. 5 for arctic through tropical conditions), it would cool sufficiently rapidly not to boil at all. Regulation of RVP does not ensure that all aviation gasoline will have the same vapour-locking or vent-loss properties, but it does ensure that differences between gasolines meeting the specifications will be small.

Specific Energy and Density

These two physical characteristics are conveniently considered together. In so far as the engine is concerned, its power output at a given mixture strength depends on the weight of air it consumes and therefore on the weight of fuel, and this on the total energy input expressed in joules per gram. However, the complete aircraft may be limited in the total amount of fuel it can carry to execute a given mission in one of two ways. It can be 'weight limited', i.e. the payload may be such that the permitted all-up weight of the aircraft is reached with less than full fuel tanks. In this instance range can be extended by using a fuel with maximum heat content per gram. Alternatively, it may be 'volume limited' in that with full fuel tanks and maximum pay load the total weight is less than that permitted for take-off. Clearly, in this circumstance, range can be extended by using a fuel with maximum heat energy per gallon. In general, the lower the density of a hydrocarbon fuel the higher is its heat content per gram and the lower its heat content per gallon.

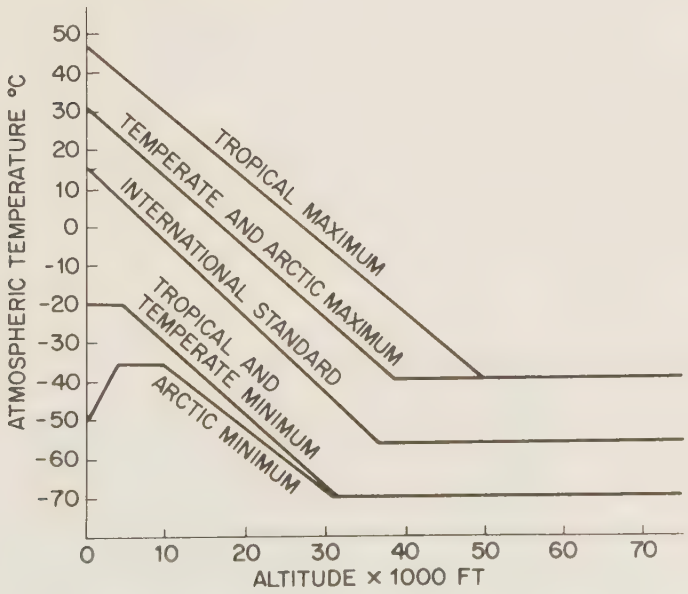

Fig. 5. Standard altitude/temperature relationships (ICAO).

Other significant properties are associated very closely with density. Distillation limits rise with increased density. Carbon:hydrogen ratios for the mixture of hydrocarbons in a conventional fuel should be low to give minimum carbon deposit and maximum heat energy. This low ratio is best met by the lower paraffins and isoparaffins. These interrelated properties of gasolines thus result in a low density trend. However, the changes in density permissible (while still meeting other requirements) are so small that for gasoline the beneficial effects accruing from the highest heat energy per gallon would only be marginal for very long-range volume-limited aircraft.

The density is not defined in gasoline specifications, being effectively qualified by stipulating minimum net heat content (in J/g). See Table 1. Determination of the specific energy is made in the standard bomb calorimeter (IP 12). Routine check values are normally calculated from the 'aniline-gravity' constant. (The product of aniline point in degrees fahrenheit and the API gravity gives a figure from which an estimate of the specific energy can be made by use of a table or by use of equations in ASTM D 1405/IP 193.) This is a simple calculation to make and is accepted in specifications in lieu of 'observed' bomb results, except for referee determinations.

The heating value is not of practical significance in gasolines, unless fuels to be compared have about the same performance number. A high heating value in a poor PN fuel cannot be fully utilized, owing to the onset of knock if the mixture is weakened to take advantage of it for a lower cruising specific consumption.

Freezing Point

The freezing point of aviation gasolines must not be higher than −60°C. It is defined as that temperature at which crystals of solid hydrocarbons formed on cooling the fuel just disappear as the fuel temperature is allowed to rise. Freezing point is determined by the joint method ASTM D 2386/IP 16. These very small crystals could cause obstruction of fuel lines and filters should they occur, but in practice all aviation gasolines now have freezing points considerably below −60°C. The requirement was originally included in specifications to prevent addition of excess benzol to the fuel to improve its anti-knock rating, for this rapidly raises the freezing point. Benzol is now excluded from aviation grades for other reasons, but the test has been retained to safeguard high-altitude performance.

Flash Point and Explosivity

The very volatile constituents present in aviation gasoline are capable of providing a flammable vapour at temperatures well below ambient. The flash point cannot be determined by any standard method. It is, however, particularly important to appreciate that even at very low temperatures the vapours present over a gasoline surface can constitute a serious explosion risk, both for bulk static storage and for the fuel contained in an aircraft tank.

Every hydrocarbon has a flammability range, that is, a range of air:fuel vapour ratios in which ignition, once started by a spark or naked flame, can

spread through the vapour space away from the flame source. High concentrations of vapour are too rich to burn and lower concentrations too weak. The limits of flammability are very much dependent on the practical conditions of test, e.g. temperature, pressure, direction of flame propagation, and ignition energy. In one test method the flammability range for methane vapour can be 5.5:14, air:fuel ratio; for ethane vapour 3:12, and so on. (An increase in temperature of the mixture will further spread these limits as also will an increase in pressure.)

For aviation gasolines these temperature and pressure effects can be expressed in the form of flammability limits in terms of altitude and fuel temperature as shown in Fig. 6.

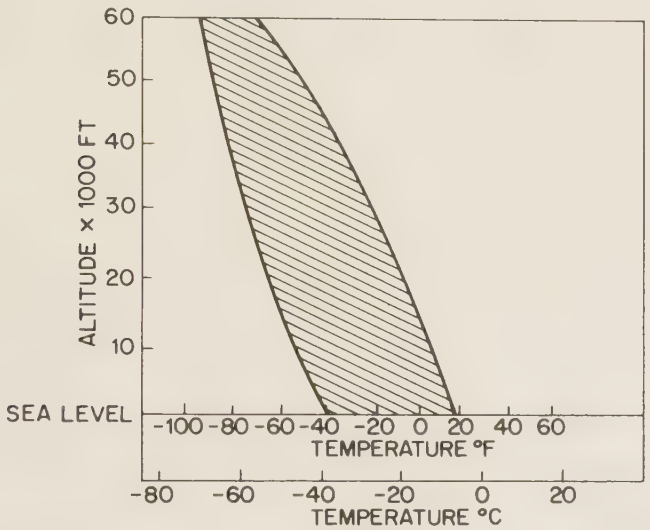

Fig. 6. Change of vapour flammability limits with altitude; average aviation gasoline (RVP = 41.5 kPa.)

Water Solubility

Specifications contain a requirement that aviation gasoline shall not lose or gain in volume more than a very small percentage when shaken with water.

The standard test requires that, when 80 ml of fuel and 20 ml of water are agitated together at room temperature, they shall separate to a sharply defined interface after a settling period of 5 minutes, with a permissible volume change not exceeding 2 ml for either fluid. There shall be no scum or bubble effect visible at the interface. Owing to the constitution of modern aviation gasolines, the limit of volume change is never encountered except in conditions of gross contamination. The more significant part of this test is now concerned with the interface condition, for the presence of scum or lace can give rise to malfunction of filter/separator equipment used in fuel handling.

Storage Stability

Aviation gasolines must be able to retain their specification properties for long periods of storage varying from arctic to tropical conditions. Unstable fuels can produce two major unacceptable effects:

(1) The deposition of solid materials within the fuel during extended storage leading to subsequent blocking of filter and metering equipment;
(2) A loss of anti-knock rating due to the change of TEL from the gasoline-soluble form to an insoluble whitish powder.

The gum compounds which can be present or produced in the fuel are classified into two types for test evaluation. 'Existent' gum may be already formed in the fuel and can be deposited from solution on inlet ports and valves and other parts of the inlet manifold as the fuel evaporates. If present, it usually gives rise to inlet valve sticking and a decrease in supercharger performance. 'Potential' or 'accelerated' gum may be formed under extended storage conditions, and is determined in the laboratory by an accelerated oxidation test in which unstable hydrocarbons are thereby polymerized and oxidized to form gums. The gum limits established for these tests ensure satisfactory storage behaviour of specification gasolines under tropical conditions for at least two years, and considerably longer in temperate climates.

The greater inclusion of reformed stocks in aviation gasoline (as distinct from straight-run gasolines) and concentrations of up to 5.5 ml TEL/gal in current high-grade fuels necessitate the addition of an anti-oxidant to achieve the gum specification figures and also to improve the TEL stability. With such inhibited fuels it is now very rare to encounter deposits due to gum or TEL degradation.

The anti-oxidants currently approved are shown in Table II. The approved anti-oxidant, or mixture of anti-oxidants is added in order to retard the formation of gum and the precipitation of lead compounds. The total weight of active material(s) must not be less than 6.7 lb nor more than 8.4 lb/35 000 UK gal of fuel (19.1 to 24.0 mg litre).

A form of instability occasionally encountered and revealed by deposits, often accompanied by colour change of the identifying dye, is associated with

TABLE II
Anti-oxidants

The following anti-oxidants are approved for use in aviation gasoline:	
(a)	2,6 ditertiary-butyl-phenol
(b)	2,6 ditertiary-butyl-4-methyl-phenol
(c)	2,4 dimethyl-6-tertiary-butyl-phenol
(d)	75 per cent min, 2,6 ditertiary-butyl-phenol
	25% max, mixed methyl and di-methyl-tertiary-butyl-phenol
(e)	55% min, 2,4-di-methyl-6-tertiary-butyl-phenol
	15% min, 4 methyl-2,6-di-tertiary-butyl-phenol
	30% max, mixed methyl and di-methyl-tertiary-butyl-phenol
(f)	72% min, 2,4-di-methyl-6-tertiary-butyl-phenol
	28% max, mixed methyl and di-methyl-tertiary-butyl-phenol
(g)	60% min, 2,4-di-tertiary-butyl-phenol
	40% max, mixed tertiary-butyl-phenol

storage under reducing conditions such as in galvanized drums. This is caused (particularly in hot climates when the fuel is more likely to be damp) by loss of the ethylene dibromide scavenger in the TEL fluid. Galvanized drums should therefore never be used for storage of aviation gasolines.

It is the practice to check all aviation gasoline stocks containing lead compounds every six months for lead instability. In this test the fuel is incubated in the dark for seven days at 49 °C in a vented glass bottle, and then visually inspected and examined for lead precipitation.

Viscosity

This property is not limited in aviation gasolines by specification. The average viscosity will be in the order of 0.75 cSt at 0 °C. It does not vary significantly from grade to grade or within each grade. Knowledge of its values with temperature change is necessary to ensure adequate flow conditions from tanks to engines, and in the design of injection nozzles for fuel injection systems.

CHEMICAL COMPOSITION OF AVIATION GASOLINES

Aviation gasolines consist almost entirely of hydrocarbons, i.e. compounds containing carbon and hydrogen only. These compounds have the highest heat content per unit weight of any conventional fuel possessing the other desirable characteristics discussed in the following sections. It is mainly on the grounds of heat energy content that other compounds such as alcohols and ethers have been rejected, for aircraft performance is greatly influenced by weight and space factors.

Crude oil contains very many hydrocarbons, and their chemical and physical characteristics are largely governed by the number of carbon and hydrogen atoms in each molecule and the manner in which these atoms are arranged within the molecule itself. Some of these arrangements and quantities have been found to be highly suited for piston engine operation, others to be deficient in essential properties and thus to be avoided or reduced in the fuel. Many of the most desirable hydrocarbons do not occur to a large extent in straight-run fuels and special refinery processes are needed to produce them.

The very many hydrocarbons occurring naturally in crudes can be grouped into three main series or types of compound, the paraffins and isoparaffins (general formula C_nH_{2n+2}), the naphthenes (C_nH_{2n}), and the aromatics (C_nH_{2n-6}). The amounts of each type present will in general vary with the crude source. The refinery operations to make a finished gasoline may vary with different crudes. Generally, however, aviation gasoline will consist of a high percentage of isoparaffins and smaller percentages of naphthenes and aromatics. A typical ultimate analysis of aviation gasoline is 84 per cent hydrogen, 15 per cent wt carbon, with some sulphur, lead, bromine, nitrogen and oxygen from dye and inhibitor, and dissolved water.

The characteristics of the three basic hydrocarbon series are given quantitatively in Table III in terms of heat content, anti-knock value, stability, and volatility. The desirable levels of performance being impossible to obtain by straight distillation, processes such as alkylation, catalytic reforming, and

TABLE III
Hydrocarbon Series Characteristics

Hydrocarbon	Heating value		Anti-knock value		Stability	Volatility
	per g	per gal	Weak	Rich		
Paraffins	Very good	Fair	Poor	Poor	Very good	High
Isoparaffins	Very good	Fair	Very good	Good	Very good	Good
Naphthenes	Good	Good	Fair	Good	Good	Variable
Olefins	Good	Poor	Poor	Variable	Poor	Variable
Aromatics	Poor	Very good	Good	Good	Good but adverse effects on sealing materials	Low

fluid catalytic cracking have been evolved to provide the necessary quality and quantity requirements for high-performance fuels.

Aviation gasolines of the higher grades require a predominance of high-octane components which do not exist naturally, but which are made available through a variety of processes within the refinery. The most important of these with regard to aviation gasolines are:

(1) The alkylation process in which unsaturated C_4 hydrocarbons, obtained from cracked gases, are reacted with isobutane, giving a highly iso-paraffinic product;
(2) Aromatization of naphthenic fractions to produce aromatic hydrocarbons possessing excellent rich-mixture anti-knock ratings.

Alkylate produced from (1) above is deficient in volatility and distillation characteristics, and isopentane is added to improve these qualities. The combination of alkylate and isopentane known as alkylate blending agent is probably the most important source of high anti-knock synthetic components for blending. The base stock, gasoline with which the synthetics are blended, consists of straight-run fractions of high initial octane number and lead response. The unsaturated compounds, the olefins, which are present in cracked stocks, cannot be used as they are unstable and prone to gum formation.

Final blending is a most important refinery operation, for selection of the proportions of the various components must be made to give a balanced and economic product meeting the specification requirements. The poor mixture response of the paraffinic alkylates must be balanced by the inclusion of some aromatics, and similarly the low volatility of most synthetic blending agents by the addition of the more volatile compounds. Overall there is the problem of availability and maximum utilization of refinery component products.

BOOST FLUIDS

Boost fluids are used to augment engine power at take-off conditions. It has been mentioned earlier that, when a supercharged engine is operated at high boost, the mixture has to be enriched to keep the engine operating condition knock-free (Fig. 2). This extra fuel cools the cylinder walls and the charge, thus

delaying the onset of knock which would otherwise occur at the associated higher temperatures. Various fluids and mixtures have been investigated as possible cheaper and more effective coolants and, in particular water, ammonia, and methanol. Water is prone to icing difficulties, ammonia can give rise to corrosion, while neat methanol carries the risk of explosion. A combination of water and methanol has been found to be the most effective coolant, and two concentrations are in general use.

The British specification D.Eng.R.D. 2491 stipulates a 60/40 methanol/water blend. This blend has minimum corrosive action on light alloy and a freezing point of −60°C, equal to the freezing point maximum of aviation gasoline. The overall effect of boost fluid injection is to permit a considerable increase in knock-free engine power to be developed for the same combustion chamber temperature, this power increase being obtained from the higher allowable boost. In practice, the fuel mixture is usually weakened when using boost fluid injection, and the ratio of the two fluid flows is approximately 100 parts of fuel to 25 parts of fluid. The resulting performance with such a ratio corresponds to an effective uprating of the fuel rich mixture rating by about 25 per cent, irrespective of its original value. The extent of power boosting is limited to about 40 per cent in practice (assuming adequate mechanical strength) for beyond this value drowning of the engine by excessive liquid is possible and balanced distribution of the fluid through the manifold to each cylinder becomes difficult to achieve.

AVIATION TURBO-FUELS

The original development of the jet engine was carried out using illuminating kerosine as the fuel. This was done to reduce the fire hazard in high-pressure fuel systems, to conserve valuable gasoline stocks in wartime and, of course, because of its ready availability. Other fuels, such as gasolines, were evaluated with regard to jet engine operations, and were found to be satisfactory with respect to combustion, ignition characteristics, and engine life, as well as being compatible with the fuel handling systems. During the course of this development it became apparent that the engine itself was non-critical, but that the environmental requirements such as pumpability at low temperatures and ease of relighting at altitude were the important quality controlling factors. These requirements led to the choice of a kerosine type of fuel as the principal fuel for gas turbine engines.

With continuing development, the engine and its control system increased considerably in complexity, and at the same time the flight envelope increased beyond the limits of the normal piston-engined aircraft. This eliminated aviation gasoline as a fuel for jet engines, because of its lower density, causing reduced range for an equivalent volume of fuel, and because of its high evaporation rate from atmospherically vented wing tanks at high altitudes. To meet this situation three main categories of turbo-fuels were evolved, ranging from low flash-point wide-cut distillate products to high flash-point narrow-cut kerosine type materials.

The wide-cut fuels consist of mixtures of naphtha and kerosine, and were introduced for military purposes to give the maximum volume percentage on crude oil (up to 40 per cent). This is to ensure availability of jet fuel in a time of

TABLE IV
Typical Aviation Turbo-fuels Specifications

		Wide cut DERD 2454 AVTAG/FSII* NATO F-40 (US JP-4)	Kerosine DERD 2453 AVTUR/FSII* NATO F-34 (US JP-8)	Kerosine DERD 2494 AVTUR NATO F-35 (ASTM JET A-1)	Kerosine DER 2452 AVCAT/FSII† NATO F-44 (US JP-5)	Kerosine joint fuelling check list JETA-1
Composition						
Total acidity, mg KOH/g	max	0.015	0.015	0.015	0.015	0.015
Aromatics, % vol	max	25.0	22.0	22.0	25.0	22.0
Olefins, % vol	max	5.0	5.0	5.0	5.0	5.0
Sulphur, total, % mass	max	0.30	0.30	0.30	0.30	0.30
Sulphur, mercaptan, % mass	max	0.001	0.001	0.001	0.001	0.001
Volatility						
Initial boiling point, °C		Report	Report	Report	Report	Report
Fuel recovered						
10% vol at °C	max	Report	205	205	205	205
20% vol at °C	max	145	Report	Report	Report	Report
50% vol at °C	max	190	Report	Report	Report	Report
90% vol at °C	max	245	Report	Report	Report	Report
End point, °C	max	270	300	300	300	300
Flash point, °C	min		38	38	60	38
Density at 15°C kg/l	min	0.751	0.775	0.775	0.788	0.775
Density at 15°C kg/l	max	0.802	0.830	0.830	0.845	0.830
Reid vapour pressure at 37.8°C kPa	min	14				
	max	21				
Fluidity						
Freezing point, °C	max	−58	−47	−47	−46	−47
Viscosity at −20°C mm^2/S	max	—	8.0	8.0	8.8	

Combustion						
Specific energy net, J/g	min	42 800	42 800	42 800	42 600	42 800
or Aniline gravity product	min	5 250	5 250	5 250	4 500	5 250
Smoke point, mm	min	21	20	20	20	19
and naphthalenes, % vol	max	—	3.0	3.0	—	3
Corrosion						
Copper classification	max	1	1	1	1	1
Silver classification	max	—	1	1	1	1
Stability						
Thermal stability (JFTOT)						
Filter pressure						
differential, mm Hg	max	25.0	25.0	25.0	25.0	25.0
Tube rating visual‡		Less than 3	Less than 3	Less than 3	Less than 3	Less than 3
TDR spun‡	max	17	17	17	17	—
Contaminants						
Copper μg/kg	max	150	150	150	150	150
Existent gum, mg/100 ml	max	7	7	7	7	7
Water reaction						
Interface rating	max	1b	1b	1b	1b	1b
Separation rating	max	2	2	2	2	2
WSIM						
Fuel with static dissipator additive	min	§	§	70	70	70
Fuel without static dissipator additive	min	70	70	85	85	85
Conductivity						
Electrical conductivity, pS/M	min	100	100	50	—	50
	max	600	600	450	—	450

* These fuels still contain between 0.10 and 0.15 volume per cent of fuel system icing inhibitor conforming to NATO Code No. S-748 and an approved corrosion inhibitor/lubricity improving additive as listed in Approved Products List 2461 (APL 2461).

† This fuel shall contain between 0.12 and 0.15 volume per cent of fuel system icing inhibitor conforming to the Joint Service Designation (JSD) AL-41.

‡ Conditional on no 'Peacock' or 'Abnormal' colour deposits.

§ Although the WSIM of the fuel containing a static dissipator additive is not limited the fuel must have a WSIM of 85 minimum prior to the addition of both the static dissipator additive and the corrosion inhibitor/lubricity improving additive.

hostilities. Kerosine types of jet fuel have a lower yield on crude (6 to 20 per cent depending on the crude source) and fall into two categories. The first, and largest, has a flash point of 38°C minimum and is used by civil airlines. The second has a high flash point (60°C min) and was evolved for use on aircraft carriers to reduce the operational hazard of fuel storage. There are in existence today a large number of jet fuel specifications, but the vast majority of these are variations of the 38°C flash point kerosine type fuel. These specifications are the purchasing specifications of major airlines, and reflect the view of the engine manufacturer as to the most desirable fuel characteristics for their own equipment. Typical aviation turbo-fuel specifications are shown in Table IV.

TURBO-FUEL SPECIFICATIONS

The first turbine fuel specification in the UK was the RDE/F/KER issued in 1943. In 1947 the first AVTUR specification was published, designated D.Eng.R.D. 2482. This satisfied the requirements of the time and stipulated a maximum specific gravity (0.81), a maximum sulphur content (0.1 per cent wt), a maximum freeze point −40°C, a high heat of combustion of 18 500 Btu/lb minimum, as well as 12 per cent vol minimum on total aromatics content. As jet engines have developed so the quality of the fuel required has changed, and this has been reflected in considerable changes in the specification. The major specification changes are shown in Table V. The chief development has been concerned with the combustion characteristics of the fuel and the fact that, as it is used as a heat-sink medium, it must be thermally stable. Another factor that became important as the fuel became more critical was fuel cleanliness. This has resulted in the strict control of particulate matter and free water in aircraft fuel tanks.

TABLE V

Specification Changes Reflecting Engine/Airframe Requirements

		1947 D.Eng.R.D.2482	1982 DERD 2453
Specific gravity, 60/60°F	max	0.810	—
Density at 15°C, kg/l	max	—	0.830
Sulphur, total, % mass	max	0.1	0.30
Aromatics, % vol	min	12	Not specified
	max	Not specified	22.0
Heat of combustion/ specific energy	min	18 500 Btu/lb	42 800 J/g (18 400 Btu/lb)
Thermal stability (JFTOT)		Not specified	
Pressure drop, mm Hg	max		25
Tube rating			<3
Electrical conductivity, pS/m	min	Not specified	100
	max		600
Additives		None specified	Anti-oxidant static dissipator FSII Corrosion inhibitor/ lubricity improver

As the development of jet engines and aviation turbo-fuels has proceeded various problems have arisen. Extra specification tests have been added in an attempt to control these problems. Most of the development effort has been, not unnaturally, directed towards improved combustion efficiency and improved specific fuel consumption. This has resulted in more thermally stable fuels, which are more highly refined than their predecessors, and this in turn has caused problems in the aircraft fuel handling systems before the fuel gets to the combustion stage. The rapid increase in aircraft size and operational range has also brought its problem of higher refuelling rates into aircraft, with the consequent generation of static electricity. These problems will be dealt with in more detail under specific headings.

In the last few years another problem has arisen, availability. Since the 1973 oil crisis there has been a growing awareness that hydrocarbon fuels have a finite life. Environmental controls have been imposed as well as conservation. This has significantly affected the distribution of products from a barrel of crude oil. At the same time jet fuel has been the one increasing product from the barrel, and hence at times has been in short supply.

Means have been tried to make more jet fuel available—make it from different crudes; this has led first to relaxing the specification by increasing the aromatic content and decreasing the smoke point, and more recently by raising the freezing point from $-50^{\circ}C$ to $-47^{\circ}C$. The latter move, although it looks a small change, has the potential to increase the total volume of fuel available for jet fuel by some 10 per cent.

Another proposed change in the specification is the use of hydrogen content as the main combustion parameter ultimately replacing aromatic/olefin contents and smoke point. This was brought about by the development of the Newport Analyser, a low-resolution nuclear magnetic resonance spectrometer, which is simple and quick to operate and determines the total hydrogen content with great accuracy. Although this method has been raised to a joint ASTM/IP test standard there is some opposition within the aircraft industry which precludes its use in specifications as the combustion parameter. One of the main points of contention is that engine combustor liner temperature is a critical engine parameter. Its direct accurate measurement is extremely difficult. Engine manufacturers have their own correlations of liner temperature with fuel aromatic content and smoke point parameters, and some are loath for these measurements to be replaced by total hydrogen content.

Fuel Characteristics

Fuel characteristics are defined by specifications, and fuel quality is controlled by fuel inspections carried out by the prescribed methods (full details of the test methods are available in either 'IP Standards for Petroleum and its Products' the ASTM 'Standards on Petroleum Products and Lubricants', or the US Federal Test Methods Standard 791). The number of test methods approved on an international basis is steadily increasing as more ASTM/IP joint methods are published.

The fuel characteristics that are important, and which are limited by specifications, can be divided into four main categories: chemical properties, physical properties, thermal properties, and storage handling.

Chemical Properties of Turbo-fuels

A prime characteristic of a turbo-fuel is that it shall be stable, clean burning, and non-corrosive to the materials of construction of the aircraft engine and airframe. Turbo-fuels are distillate fractions derived from crude petroleum and consist predominantly of hydrocarbons. The minor constituents, non-hydrocarbons, consist of sulphur, nitrogen, and oxygen in the fuel, and traces of particulate matter and water (moisture) as contaminants. The hydrocarbons may be split into four types, paraffins, olefins, naphthenes (cycloparaffins), and aromatics. The distribution of these hydrocarbon types will vary with the crude source. An approximate distribution is as follows:

Paraffins	33–61 per cent vol
Olefins	0.5–5 per cent vol
Naphthenes	10–45 per cent vol
Total aromatics	12–25 per cent vol

It can be seen that paraffins and naphthenes are the major components in jet fuels, their ratio varying with crude source. Middle East, North African, and North Sea crudes have naphthene contents at the lower end, whereas in the South American crudes naphthenes tend to the upper half of the scale.

Paraffins have a high heat of combustion on a weight basis, with naphthenes slightly less and aromatics the lowest. However, when heat of combustion is considered on a volume basis, the order is changed, with monocyclic aromatics having higher values than paraffins, which in turn are marginally higher than naphthenes.

Aromatics have a more luminous flame than paraffins and cause smokiness and carbon deposition. They are also better solvents than paraffins, and hence cause many elastomers present in fuel hose lines to swell. For these reasons an upper limit to the amount of aromatics is set in specifications. This is usually 20–25 volume per cent. Special military fuels, such as the US fuel JP-7 designed for high heat of combustion (or specific energy) on a weight basis, need to be high in paraffins, and so have a 5 volume per cent maximum aromatics content.

Aromatics are present in turbo-fuels principally as monocyclic hydrocarbons, although polynuclear aromatics, essentially two- and three-ring compounds, do occur in small quantities. These polynuclear aromatics contribute to highly luminous flames giving high radiant heat in the combustion chamber. They are also good 'lubricity' agents for control valves and fuel pumps in the fuel-handling system, which rely entirely on the fuel for lubrication. Modern refinery processes producing highly refined turbo-fuels, especially those involving hydrotreating, tend to remove polynuclear aromatics. This is advisable from a combustion point of view, but possibly not from the fuel handling systems standpoint. The phenomenon of fuel lubricity has manifested itself in several ways over the past fifteen years. The most critical portion of the fuel system to lubricity is the high-pressure fuel pump which is entirely fuel lubricated. The highly refined very clean fuels produced today do not always have the lubricity which their predecessors did. This tends to increase the wear on the pump and so reduces its life. Also in the last fifteen years the life expectancy of aircraft engine equipment has increased very significantly, and so one now tends to expect a 10 000 hours pump life between overhauls, whereas 2000 hours was acceptable in the late 1960s.

As engines have become more efficient fuel pressures have tended to rise and fuel systems have become lighter to save on overall weight. This has tended to shorten the operating life of both piston and gear pumps. Work by the manufacturers has shown that a mechanical modification to the pump, usually a change in metallurgy, can be made to overcome this problem. It has also been shown that a small quantity (10–12 ppm) of an approved corrosion inhibitor added to the fuel will protect the original systems. Various attempts have been made to devise a laboratory test to control the problem. One such test is the Ball-on-Cylinder rig. In this a cylinder rotates through the test fuel and has a ball mounted on top of it. The rig is run under controlled conditions and at the finish the mean wear scar diameter on the ball is measured. This test gives quite a good correlation as to how that fuel is likely to behave in an engine fuel system. Attempts to get good reproducibility between operators to make it a standard test have so far not been too successful. A CRC task group in the USA is currently working on this problem. By modifying the equipment and tightening up on the test procedure they hope for success. The same sort of thing has happened to other proposed tests to measure this parameter, but without success. The chemistry of lubricity or of compounds which can act as a lubricant in a fuel system is extremely complex, and indeed lubricity is difficult to define. It is for this reason that a successful test method to control such an elusive property has not yet been found. There are, however, several methods, which can evaluate lubricity and show trends from which one may make predictions. Whether a precise reproducible method which could be used in specifications is possible is doubtful, since there are so many conflicting factors. The most reasonable approach is to design fuel systems, high-pressure pumps in particular, which can run on low-lubricity fuels. This approach has been taken by the major fuel pump manufacturers in the aviation industry and very few incidents of this type are now reported.

Olefins are limited, usually to 5 per cent vol, on account of their instability, chemical reactivity, and ease with which they form gums. They have good burning qualities, and are intermediate between paraffins and naphthenes as regards heat of combustion.

Alcohols are excluded from turbo-fuels for two reasons, their affinity for water and their low calorific value.

The non-hydrocarbons present in turbo-fuels are compounds containing sulphur, nitrogen, and oxygen. The amount of sulphur and nitrogen present is controlled by the crude source composition and by the method of processing. The total sulphur content is limited; the limit varies with specifications and is generally 0.3 per cent wt maximum and never greater than 0.4 per cent wt. This upper limit is probably debatable from a technical point of view; it does, however, restrict the amount of corrosive combustion products, sulphur dioxide, and sulphuric acid, present in the combustion chamber and turbine section of the engine. It is also a control on exhaust emissions and environmental control of the atmosphere, now an important factor.

In the presence of the sulphur compounds even stable fuels are capable of absorbing oxygen when subjected to heat. Continued heating can also cause the primary oxidation products to be further oxidized, the reaction rate increasing with time and temperature. The end result of these reactions is the precipitation of a solid phase insoluble in the fuel. To ensure that turbo-fuels do

not react in this way the total sulphur and mercaptan sulphur contents of the fuels are strictly controlled, as well as the thermal stability (described later) and gum content. (Gums, hard varnish-like deposits are known to contain large amounts of sulphur.)

Mercaptan sulphur is controlled specifically for its corrosiveness to copper and cadmium, and for its disagreeable odour. The specifications limit the amount of mercaptan sulphur to less than 0.003 per cent and in many cases to less than 0.001 mass per cent.

Mercaptan sulphur and/or other complex corrosive compounds are also limited by a copper strip corrosion test, which defines the maximum stain that the strip may have after being heated in the fuel at a set temperature for a set time. As a further protection against sulphide corrosion on silver parts, present in some fuel pumps, a similar type of test has been introduced using a silver strip. These tests are complementary. In the last decade new equipment has been introduced into aircraft fuel systems without any silver parts, and so this test protects only fuel systems in the older types of engine. In time it should no longer be needed.

Nitrogen compounds occur mainly in the heavy end of the fuel and are detected in gums and sediments. The amount of nitrogen present is not limited by specifications, but is controlled by the thermal stability tests.

Oxygen, also, is not limited, except when present in naphthenic acids or phenols which are controlled by an acidity test.

As previously stated, gums contain a large amount of sulphur. They are, in fact, high-molecular-weight, non-volatile organic complexes of carbon, hydrogen, sulphur, oxygen, and sometimes nitrogen. Gum formation can take place in fuels when stored for a long time or when under thermal stress at high temperatures in modern high-speed aircraft. This latter effect can adversely affect engine performance by blocking burner jets or fouling up heat exchangers.

Fuel Additives

Oxidation inhibitors are used in turbo-fuels to prevent gum formation. Additionally, they are added to retard peroxide formation in certain hydrotreated fuels, for peroxides, if present in the fuel, will attack nitrile rubber hoses used on the fuel system of some aircraft engines.

A metal deactivator is permitted in most jet fuel specifications. This has the effect of removing by chelation, any dissolved copper that may be present in the fuel as a result of refinery processing. Copper is undesirable in the fuel as it will catalyse oxidation reactions and so help to form gums. The MDA can also form chelates with other metals such as iron; copper removal is, however, of prime importance.

An anti-icing additive is sometimes required to be added to a fuel, and is obligatory in certain specifications. Its purpose is to ensure that dissolved water in the fuel, which will tend to come out of solution as the fuel temperature drops, does not freeze in the fuel system. The use of this additive is necessary if the engine fuel system is not equipped with fuel heaters.

A static dissipator additive is now required in most fuel specifications to increase the conductivity of the fuel and so reduce the possibility of an

electrostatic discharge causing an explosion during high-speed refuelling through a micronic filter. The additive approved for use in British specifications is ASA-3 and is added in concentrations up to 1 ppm. Another additive currently under evaluation is known as Stadis 450. This additive is likely to receive full approval from the engine and airframe manufacturers in 1982. It will then be permitted in the major specifications.

Corrosion inhibitors are used in the US and for military purposes in Europe, essentially for distribution pipeline protection. They also exhibit beneficial properties with respect to fuel lubricity and as such are used by military forces.

Anti-smoke additives are available to reduce the amount of smoke emitted from jet engines on take-off. As new engines have such improved combustion efficiency they are not currently used and have never been stipulated in aviation fuel specifications. Fuel soluble biocides are used to inhibit microbial and fungoidal growth in aircraft fuel systems. With aircraft continuously flying into temperate and warm climatic areas the evidence of microbial infestation in aircraft fuel systems is increasing. As effective biocides, if used continuously, would have a deleterious effect on the engine, they are used periodically as a shock treatment. That is some biocide is added to the fuel when the aircraft is taken out of service for a periodic overhaul/inspection and left preferably for three days. This will kill any organisms and clean up the system. Back in service again the system is likely to be reinfected in time but periodic treatment of, say, once every three to four months will keep the system in a satisfactory condition.

Another approach is to add a biostat to the fuel on a continual basis. This is very effective but costly. However, if there is a need for an anti-icing additive, as mentioned above, then due to its high partition coefficient between the fuel and water it goes into the water phase in such a concentration as to be an effective biostat. Biocides/biostats are not included in fuel specifications.

Physical Properties of Turbo-fuels

Physical properties are of considerable importance with regard to engine and airframe fuel system design. They also affect storage and handling facilities, and constitute a relatively simple and effective means of controlling product quality.

Density

This is a very important parameter in the design of fuel tanks in aircraft (weight/volume loadings on the airframe).

Fuels varying over a very considerable density range can readily satisfy the essential quality requirements of a turbo-fuel. However, to get satisfactory engine control it has become necessary to limit the density of a particular type of fuel, e.g. kerosine type. The particular density limits laid down in current specifications are, in fact, a compromise between ideal engine design requirements, product availability, and cost.

Jet aircraft are used on all of the world's major trunk routes. Their fuel costs rate high amongst operating costs and the introduction of supersonic transport in the 1970s still further extended the fuel's proportion of the operating costs. As a result of this the density of the fuel, as well as being an important physical

design parameter, has become important when considering total heat (energy) content. Fuel is supplied by volume, so from a purchasing viewpoint, a high heat content per gallon, high energy per unit volume, is desirable. To achieve this the density of the fuel must be raised so that the same volume of fuel weighs more. The relationship between density and specific energy is shown in Fig. 7, and it will be noted that although the specific energy on a volume basis increases with increasing density, it decreases on a weight basis so that on the two above-mentioned considerations there is an optimum value for the density.

In practice one has to decide whether the aircraft is to be weight-limited or volume-limited. This can be done by considering route structures, traffic density and a balance between payload (which is in fact revenue) and fuel weight. The density of the fuel must be considered for a particular flight plan. On long-distance routes, in particular, the ratio of total fuel to payload must be calculated to give maximum payload with safety. It will readily be seen that with a fuel load of 20 000 gal a slight difference in density can considerably affect the final payload.

Over a wide range of hydrocarbons normally found in the kerosine fraction the specific energy per unit weight covers only a small range of values, and practical use of this range is extremely difficult owing to the complexity of producing fuels of sufficiently limited composition.

On a volumetric basis, however, specific energy can show a much wider variation associated with the density range which arises from the composition and make-up of the hydrocarbons concerned. In general over the hydrocarbon range C_8–C_{16}, the ratio of maximum to minimum energy content on a volumetric basis is some four times that on a gravimetric basis.

The cycloparaffins and monocyclic aromatic compounds with a large number of carbon atoms in aliphatic side chains have the highest heating values overall. Their distribution in a particular crude distillate fraction in fact fixes the overall heating value of the fuel.

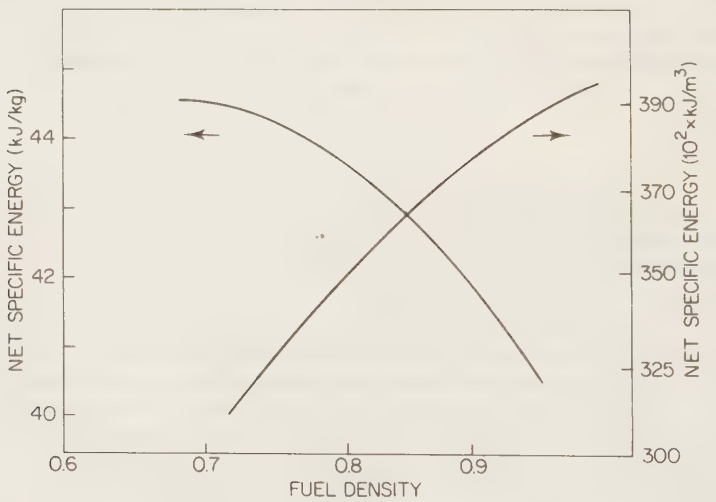

Fig. 7. Net specific energy vs density.

Viscosity

This property is specified to ensure that:

(a) Fuel line pressure losses are maintained at acceptable levels when operating at low temperatures;
(b) Fuel injection nozzles and fuel system controls will be operating at or near to design conditions.

In many commercial turbo-fuel specifications a maximum viscosity is quoted for one temperature. Most require a maximum viscosity of 8 cSt at −20°C. Viscosity is not a limiting parameter for wide-cut fuels, since other parameters such as volatility and freeze point are more critical. To define the viscosity/temperature relationship of a fuel, determination at two different temperatures is required, and this gives a straight line plot on a standard viscosity/temperature chart. Typical viscosity/temperature characteristics of aviation fuels are shown in Fig. 8. It will be noted that the slope of these lines is similar, and this characteristic is used in specifications so that viscosity requirements can be clearly defined by limiting the viscosity at one temperature only.

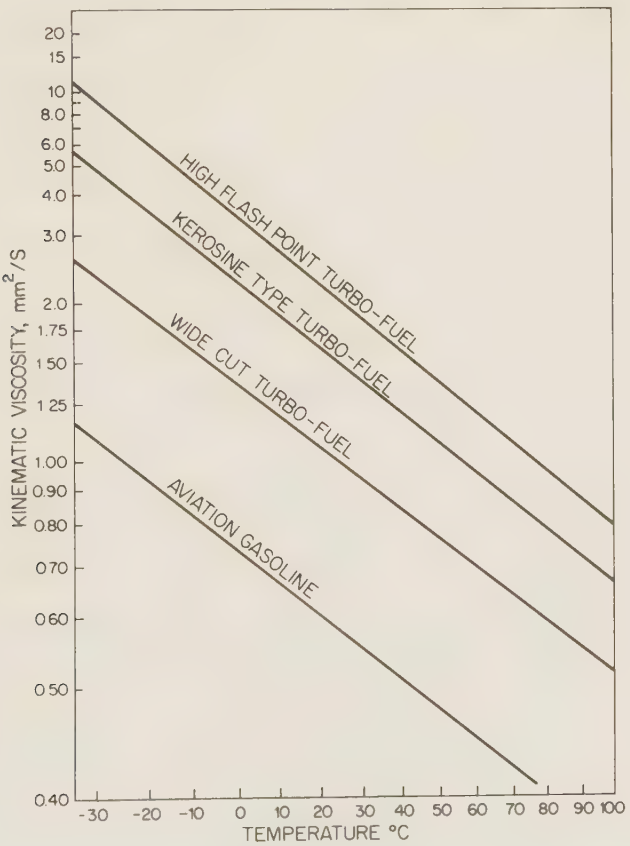

Fig. 8. Typical viscosity-temperature characteristics for aviation fuels.

The viscosity of the fuel can also affect the life of the fuel pump, as it relies on the fuel that it is pumping to lubricate its moving parts, where this lubrication is hydrodynamic. However, under certain conditions of operation boundary-layer lubrication occurs and in this situation fuel viscosity has little or no effect.

Volatility

The most important reason for controlling the volatility of turbo-fuels is the loss of fuel from unpressurized aircraft fuel tanks due to boiling-off at high altitudes. Modern jet aircraft fly at considerably higher altitudes than their piston-engined predecessors. For this reason, amongst others, the low-volatility kerosine type fuel is attractive. A typical distillation range is from 150–245 °C, the low volatility also being controlled by a flash point minimum. The flash point is primarily a safe-handling factor, but the two parameters are interrelated. To ensure a reasonable blend of fuel and to eliminate the possibility of blending stocks of widely varying boiling ranges and volatilities, 20 and 90 per cent volume minima are stipulated. The 20 per cent point controls front-end volatility, ensuring that the fuel will readily vaporize for cold starting and yet not be too volatile giving rise to high evaporation losses at high altitudes. The 90 per cent point controls the amount of high boiling point material which could affect overall engine performance.

The wide-cut fuel, still used by some military aircraft to ensure continuity of supply in times of emergency, has a flash point of about −25 °C, which is not, of course, specified. The front-end volatility of this type of fuel is controlled by Reid vapour pressure limits, and either a control on 20 per cent recovered or a control on the per cent distilled at 143 °C.

The high flash point type of turbo-fuel is essentially a safety fuel for use on aircraft carriers. Its distillation range is controlled by the fact that the fuel must meet a high minimum flash point and a maximum freeze point.

Typical distillation curves for the three types of turbo-fuels are shown in Fig. 9.

Differences in volatility have varying effects on a turbo-fuel, so that the final blend is a compromise to achieve as many desirable conditions as possible. A high front-end volatility facilitates easy engine starting and aids re-lighting at high altitude. On the other hand, it promotes fuel losses due to boil-off at high altitude and causes unsteady flow in fuel system lines in the high-temperature zones of the engine. A low front-end volatility used to cause cold-start difficulties, but these have now been overcome by the use of high-energy, low-tension ignition systems.

The problem of fuel boiling-off at high altitude is at present minimized by the corresponding low temperatures encountered at high altitudes; and hence low fuel temperatures in the aircraft fuel system. On a subsonic Transatlantic flight, for example, air temperatures down to −65 °C are likely to be encountered, resulting in fuel temperatures of −30 °C to −35 °C. At these low temperatures there is negligible fuel boil-off in spite of the low pressure. It was felt that when supersonic transport was introduced into service fuel boil-off could become a problem. The reasons were that the SST would fly higher than the subsonic transport (lower atmospheric pressure), faster (so creating high skin friction to heat the fuel) and use fuel as a cabin-air and lubricating oil heat

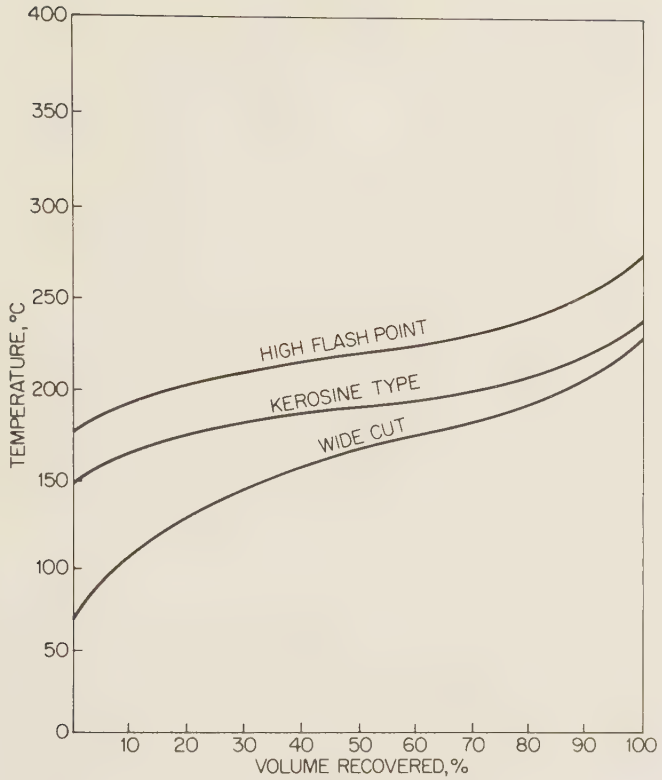

Fig. 9. Typical distillation curves–turbo-fuels.

sink. However, after several years of operation of Concorde by both Air France and British Airways this potential problem has not materialized, and they operate successfully on a normal Jet A 1 type kerosine.

Air solubility

Air solubility in kerosines obeys Henry's Law which states that the amount dissolved is proportional to its partial pressure in the vapour phase, or in other words the amount dissolved is proportional to the difference between atmospheric pressure and fuel vapour pressure. In the case of kerosine, with a very low vapour pressure, air solubility is approximately proportional to atmospheric pressure. This means that dissolved air will be evolved as the aircraft climbs, and the rate of release is controlled by the degree of agitation of the fuel.

The lower the density, surface tension, and viscosity of the fuel, the more air it can dissolve. Hence wide-cut turbo-fuels will dissolve more air than will the kerosine type. This is illustrated in Table VI.

As the aircraft climbs the reduction of external pressure decreases the solubility of air in the fuel, with the result that the dissolved air is expelled from the fuel and escapes from the tanks via the breather vents, carrying fuel vapour

TABLE VI
Solubility of Air in Fuels

Density at 20°C (kg/l)	Viscosity at 20°C (mm^2/S)	Surface tension at 20°C (mN/m)	Solubility at 20°C (% volume)
0.725	0.64	18.5	22.9
0.781	1.69	23.5	17.3
0.872	17.7	26.5	9.7

with it. Table VII shows that if the initial concentration of air in a kerosine type fuel is 11.5 per cent vol, then on climbing to 33 000 ft (10 000 m) (200 mm Hg atmospheric pressure) 8.5 per cent of the air will be expelled, leaving only 3 per cent remaining in the fuel. This means that if there were 10 000 UK gal of fuel (45 400 l) in an aircraft tank, then just over 138 cu ft of air (3860 l) could be expelled from the fuel, taking fuel vapour with it. If this air is suddenly released from a quiescent fuel by pumping vigorously, for example, this can cause considerable frothing and most probably a considerable fuel loss.

Water solubility

Dissolved water is always present in turbo-fuel, the amount varying with the relative humidity of the atmosphere above it and the temperature. Every effort is made by the supplier to remove free water from the fuel, and this is controlled on airfields by various simple go/no-go tests where the upper limit is set at 30 ppm. It is impractical to attempt to remove dissolved water, by refrigeration or by use of a desiccant, for example, as the fuel will reach a water equilibrium in a matter of hours when re-exposed to the atmosphere in a vented storage or aircraft tank.

Water is only slightly soluble in turbo-fuels (42 ppm in the kerosine type at 15°C), but exhibits a considerable decrease in solubility with decrease in temperature. Figure 10 shows the solubility of water in aviation turbo-fuels, plotting volume per cent water against temperature. With the large volumes of

TABLE VII
Liberation of Dissolved Air on Climbing

Approx. altitude (ft)	Atmospheric pressure on climbing (mm Hg)	Equilibrium concentration of air in fuel, % vol	
		Kerosine type	Wide-cut
Sea level	760	11.5	18.5
700	700	10.9	17.5
1 950	600	9.0	15.0
3 400	500	7.5	12.5
5 100	400	6.0	10.0
7 400	300	4.5	6.0
10 000	200	3.0	5.0
14 375	100	1.8	2.5

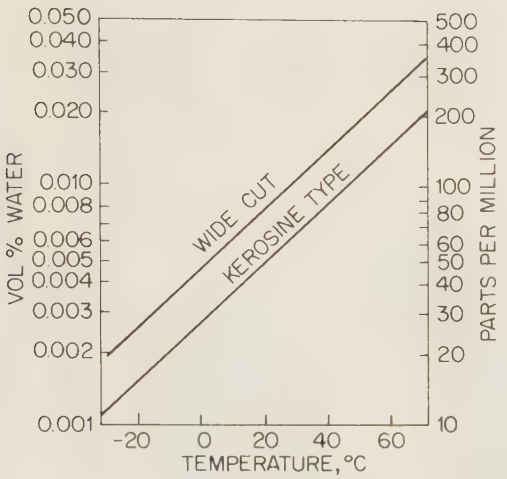

FIG. 10. Solubility of water in aviation turbo-fuels.

fuel now being carried in aircraft, significant amounts of water can be thrown out of solution in the aircraft fuel tanks as the outside temperature decreases. Again, considering 10 000 UK gal of fuel then $1\frac{1}{4}$ gal of free water can be formed for a drop in temperature of 40°C. Some of the water will settle, but much will form ice crystals in the fuel at the low temperature encountered in flight. Owing to the aircraft's movement these ice crystals rarely settle out or agglomerate in the tank, but are suspended in the fuel. For this reason fuel filters are now normally heated to maintain a constant fuel temperature through the filter, or are fitted with a device to control the minimum temperature of the fuel into the filter, usually 5°C.

Flammability

The difference in volatility between the wide-cut and kerosine types of turbo-fuel has a considerable effect on their flammability temperature limits. An illustration of flammability limits for any fuel is shown in Fig. 11.

The flammability limits define the fuel temperature region in which the fuel will release the correct amount of hydrocarbon vapour to form a flammable mixture with air.

Typical flammability temperatures for aviation kerosine are in the range 43°C to 66°C, whereas those for the wide-cut fuel are −29°C to 15°C. These limits apply only for fuels which are in equilibrium with their vapours at the given temperature. This equilibrium condition is probably true in at least part of the vapour space as a result of rapid diffusion from the fuel-wet surfaces in both ground tanks and aircraft tanks. It is important to note that temperature flammability limits refer to the temperature of the fuel in the immediate vicinity of the vapour space.

If all parts of a fuel tank and the fuel contained in it are at the same temperature, then the temperature of the bulk fuel determines whether or not the vapour is in the flammable region. In the case of an aircraft tank, and a refueller

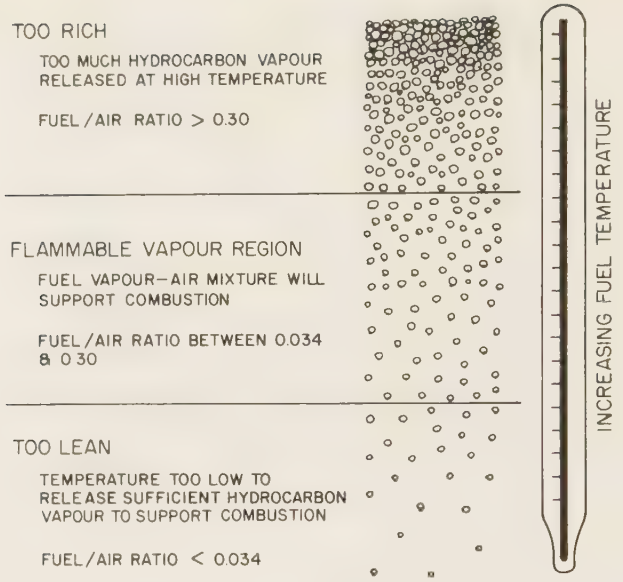
TOO RICH
TOO MUCH HYDROCARBON VAPOUR RELEASED AT HIGH TEMPERATURE
FUEL/AIR RATIO > 0.30
FLAMMABLE VAPOUR REGION
FUEL VAPOUR–AIR MIXTURE WILL SUPPORT COMBUSTION
FUEL/AIR RATIO BETWEEN 0.034 & 0.30
TOO LEAN
TEMPERATURE TOO LOW TO RELEASE SUFFICIENT HYDROCARBON VAPOUR TO SUPPORT COMBUSTION
FUEL/AIR RATIO < 0.034
INCREASING FUEL TEMPERATURE

FIG. 11. Flammability limits for aviation fuel.

tank also, the tank walls can sometimes be colder, or even warmer than the bulk fuel. Under these conditions if the tank walls are wetted by spray filling or agitation, different parts of the tank vapour space will have different vapour concentrations at a given moment in time. Thus, in estimating whether a flammable vapour exists in a system or not, all the fuel temperatures that can occur in the system must be considered. If any of the fuel temperatures lie within the flammability region of the fuel it is reasonable to assume that part, at least, of the vapour space contains a flammable mixture.

As the density of air decreases with altitude, less hydrocarbon vapour is required to form flammable mixtures with the reduced amount of air that is present. Fig. 12 shows the change of flammability limits for both wide-cut and kerosine types of jet fuel with altitude. The limits for aviation gasoline are included for completeness.

Auto-ignition

Auto-ignition of a turbo-fuel is possible as the result of drops of fuel falling on to a red-hot metallic surface. This can happen with a slight fuel leak from the engine shortly after shut-down, the fuel impinging on the hot tail pipe, or from a fuel line fracture during operation, when some fuel or fuel vapour contacts a hot component of the engine.

At what temperature is auto-ignition possible when fuel comes into contact with a hot surface? Generally in the case of aviation fuels the lighter the product (lower density) the higher the auto-ignition temperature. The actual value varies with the method of determination and the environment. The 'drop' method is widely used; droplets of fuel fall on to a hot surface and the

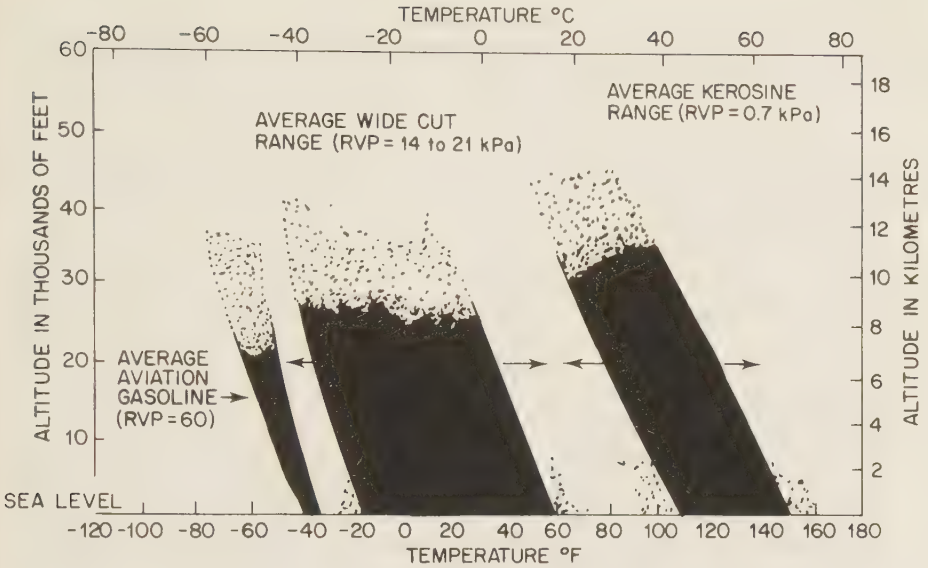
TEMPERATURE °C
-80 -60 -40 -20 0 20 40 60 80
ALTITUDE IN THOUSANDS OF FEET
60 50 40 30 20 10
SEA LEVEL
AVERAGE WIDE CUT
RANGE (RVP = 14 to 21 kPa)
AVERAGE KEROSINE
RANGE (RVP = 0.7 kPa)
AVERAGE
AVIATION
GASOLINE
(RVP = 60)
ALTITUDE IN KILOMETRES
18 16 14 12 10 8 6 4 2
-120 -100 -80 -60 -40 -20 0 20 40 60 80 100 120 140 160 180
TEMPERATURE °F

FIG. 12. Change of vapour flammability temperature limits with altitude.

temperature of the gas close to the surface of the plate is measured. The temperature at which the fuel is ignited by a slight explosion is taken as the auto-ignition temperature. Table VIII gives the auto-ignition temperatures of aviation fuels, determined in this way.

As the vapour pressure increases the auto-ignition temperature increases, but the flash point decreases. This fact explains what happens to the auto-ignition temperature with altitude. As the pressure of the atmosphere is reduced the vapour pressure of the fuel increases, and so the auto-ignition temperature increases. Table IX shows the effect of altitude on the auto-ignition temperature.

Thermal Properties of Turbo-fuels

The original interest in the thermal properties of turbo-fuels was concerned with the low temperature of the fuel to ensure that it did not freeze in the aircraft's tanks at high altitude. With the rapid development of the jet engine, however, more exacting thermal demands have been made on the fuels by the

TABLE VIII
Auto-ignition Temperature of Aviation Fuel

Fuel	Vapour pressure at 37.8°C (mm Hg)	Auto-ignition temperature in air (drop method) (°C)
Kerosine type	25	228
Wide-cut	100	242
Aviation gasoline 100/130	360	440

TABLE IX

Effect of Altitude on the Auto-ignition Temperature of Aviation Fuels

Fuel	Vapour pressure at 37.8°C (mm Hg)	Auto-ignition temperature (°C)	
		Atmospheric pressure	
		742 mm	370 mm
		Altitude	
		200 m (700 ft)	5 700 m (18 700 ft)
Kerosine type	25	228	444
Wide-cut	100	242	449
Aviation gasoline 100/130	360	440	553

expansion of flight operation conditions, and by new uses being made of the fuel. Long flight duration at high-altitude (low-temperature) conditions, using kerosine type fuel necessitated the use of fuels which have low freezing points and maintain their flow properties. Fuels are now used as a heat sink medium for the lubricating oils, via a heat exchanger, and so their thermal stability at elevated temperatures has become important. With the advent of supersonic aircraft, fuel is used as a heat sink for the cabin air conditioning system as well. On the supersonic aircraft (SST) there is a considerable aerodynamic heating effect, which under Mach 2.0 conditions (Concorde), can raise the temperature of the residual fuel in the tanks to 85°C. Fuels for the SST will require a high degree of thermal stability, otherwise deposits and lacquers will be formed in the heat exchangers, and in the fuel tanks. Current Jet A-1 fuels have this high thermal stability, and so Concorde is able to operate on the aviation fuel available at all major airports.

Another thermal property of increasing significance is the radiant heat emitted in the combustion chamber of the engine and its effect on the life of the hot parts of the engine. This property is controlled by the luminometer number or partially by smoke point.

Low-temperature properties

The main criteria for a freezing point limit are the ability of the fuel (a) to be pumped, and (b) to flow effectively through the fuel handling system. Most fuels can be pumped below their freezing point, but there is always the danger that the wax crystals and ice crystals from water that has come out of solution, will clog and block filters, preventing fuel flow. On most aircraft fuel filter heaters are normally fitted for ice prevention and this reduces the problem of filter plugging. Fuel flow failure, in this case, occurs when the pump fails to get suction because of the inability of the fuel to flow into the fuel pump inlet. Although the fuel will flow below the freezing point, it is safe practice to work with a fuel that has a freezing point below its expected operating temperature.

Wide-cut turbo-fuels universally have a freezing point specification of −60°C maximum, and for all foreseeable operations this limit is completely acceptable.

With kerosine type aviation turbine fuels the freezing point varies from −47°C maximum for Jet A-1 to −40°C maximum for Jet A fuel. It is considered unlikely that a fuel with a freezing point below −47°C will be required.

With the advent of pure jet subsonic passenger aircraft in the late 1950s, cruising at around Mach 0.8, the flight times at high altitude of commercial aircraft were reduced significantly. Since then the wide-bodied jet aircraft came into service in the late 1960s and their range was increased during the 1970s, so that once again aircraft are flying non-stop for 10–12 hours at altitudes of 30 000 to 35 000 ft. At this altitude they are flying in very low outside air temperatures necessitating good low-temperature properties of the turbo-fuels.

For many years international airline operators used the Jet A-1 type fuel (DERD 2494) with a freezing point maximum of −50°C, and within the USA the operators used a Jet A kerosine type fuel with a maximum freezing point of −40°C. Since the 1973 fuel crisis there has been growing pressure to raise the freezing point maximum of Jet A-1 in order to make more jet fuel available from a barrel of crude oil. The freezing point parameter is a very significant one in affecting the yield of jet fuel from a particular crude oil because it, in practice, controls the final boiling point. This effect is very significant with waxy crudes such as those from the Middle East. An example of this is illustrated in Fig. 13 for a paraffinic Middle East crude.

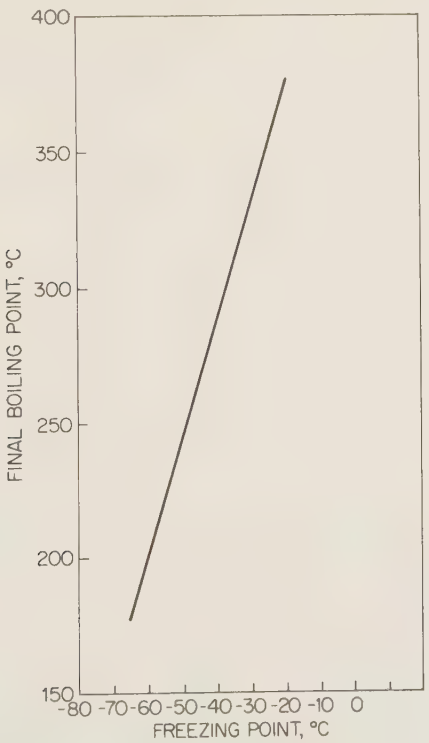

Fig. 13. Effect of freezing point on final boiling point.

In the mid-seventies surveys were carried out by the major airlines for the International Air Transport Association (IATA) to determine the actual fuel temperatures in the wing tanks during long-distance flights. The result showed that all international routes could operate successfully on current flight patterns with a slightly less restrictive freezing point turbo-fuel. These data are calculated so that statistically the fuel freezing point will not affect the flight plan on more than one day per year. When that time comes they have to vary their route plan to avoid the cold air by going round or flying lower.

The consequence of this was that the Jet A-1 type kerosine fuels in 1980 changed from a $-50\,^{\circ}C$ maximum freezing point to $-47\,^{\circ}C$, with a consequent increase in availability.

With the longer flight times of the wide-bodied jet airliners very low fuel temperatures are encountered on a few of the world's routes, but to date the use of $-47\,^{\circ}C$ freezing point maximum fuel has not affected flight plans.

High-temperature properties—thermal stability

Fuel now constitutes a considerable portion of the load on large inter-continental aircraft. It has a considerable heat-sink capacity and, as such, is used as a coolant for engine oil, hydraulic and electronic equipment. On high-speed military aircraft and on supersonic transports the fuel is also used as a heat sink for the air-conditioning systems and in the control of cabin air temperatures. On top of this heat absorption at supersonic speeds there is considerable kinetic heating. In receiving all this heat it is of paramount importance that the fuel does not oxidize and form gums, varnishes, and deposits which will affect the efficiency of the heat exchangers, and also be liable to clog fuel filters, fuel meters, or fuel injection nozzles into the combustion chambers.

The direct controls of gum formation and of the aromatic and olefin content of the fuel, whilst being useful controls in themselves, have not proved reliable in evaluating fuel performance at high temperatures.

The original rig which was developed to control the thermal stability of a turbo-fuel was the CFR fuel coker. It consisted of a preheater tube representing the fuel/engine oil heat exchanger and a 25 micron stainless steel filter representing the fuel injection nozzle in the combustion chamber. The fuel was passed through at a constant rate for a fixed time (6 pounds per hour for 5 hours) and the thermal stability rating was a combination of a visual tube deposit rating and a pressure drop across the filter. This test was standardized as IP 197/ASTM D 1660.

Modifications were made to the instrument and a Research Coker was produced which involved fuel preheat and increased operating temperatures. This instrument was designed to test fuels to their thermal limits and to give information of the thermal stability required of a fuel for advanced military aircraft. Although the system worked its reproducibility at high temperatures was very poor. As a result of this the Co-ordinating Research Council (CRC) in the USA set up an evaluation panel to replace the CFR coker. Several candidates were evaluated, and finally the Jet Fuel Thermal Oxidation Tester (JFTOT) was decided upon. Although in principle it resembles the CFR Coker it has many advantages over the old method. It is much more precise, has the

capability of working over a wide temperature range, and for routine and research purposes uses much less fuel. A charge of 600 ml is required as against 20 litres for the Coker, and the test time is $2\frac{1}{2}$ hours against 5 hours.

In the JFTOT a charge is placed in a reservoir and the whole system pressurised to 3.45 MPa (500 psi) with nitrogen. This is done to ensure a single-phase reaction in the heated section, that is to prevent liquid/vapour mixtures. The fuel passes from the reservoir through a 0.45 micron filter, to remove trace particulate matter which would adversely affect thermal stability, and into the reactor section, where it passes upwards in an annular space over an aluminium tube and out via a 17 micron stainless steel filter through a heat exchanger, to cool it, and back to the top of the reservoir. The used and unused fuel in the reservoir are separated by a floating piston and so do not come into contact. The fuel is rated by a visual tube rating or by placing the tube in a Tube Deposit Rater. In this the tube is rotated at a constant speed and its surface scanned by two light sources reflecting off the tube on to a photo-cell. The photo-cell gives a signal to a meter. Also the differential pressure across the 17 micron filter is measured. This test is standardized as IP 323/ASTM D 3241, and is mandatory in UK (DERD) specifications and the Joint System Check List.

The temperature at which the test is carried out to meet DERD specifications is 260 °C, but as it is an enclosed pressurized system much higher temperatures are possible without getting into a two-phase system. Because of this it becomes a useful research tool. One modification of technique is to determine the threshold thermal stability of a turbo-fuel, that is the highest temperature at which it passes the specification requirement. This can be done by running the test at a series of temperatures, say 260 °C, 280 °C and 300 °C, ensuring that the highest temperature is above the threshold limit, and plotting the TDR readings against temperature. By taking a specific TDR reading as the pass limit, 15 is the limit in DERD specifications and is being considered by ASTM, and plotting TDR against temperature the threshold temperature can be determined.

Another modification is to fit a mini-heated reservoir (MHR) between the main reservoir and the reactor section. This is simply a 230 ml container that may be heated up to 200 °C and it is fitted with a magnetic stirrer so that any deposits formed in it are kept in suspension and carried forward to the reaction tube or micronic filter. In this way fuel may be heat-soaked for one hour at a selected temperature before being rated in the normal way. Modern military aircraft thermally stress the turbo-fuel with all the cooling required by the electronic equipment, and it is very useful, therefore, to be able to predict the behaviour of a fuel in such circumstances. A schematic flow diagram of the JFTOT with MHR is shown in Fig. 14, and the equipment is shown in Fig. 15.

Various other innovations have been made for specific research purposes, but they are not in general use. Instances of these are a window in the reaction section so that the rate of deposition on the tube may be measured by a modified TDR; a flat-sided metal surface in place of the aluminium tube, so that it is easier to fit into ESCA or Scanning Electron Microscopes in order to identify the type of deposit; stainless steel reaction tubes in place of the standard aluminium tube, to ascertain the difference in thermal decomposition by changing the metallurgy.

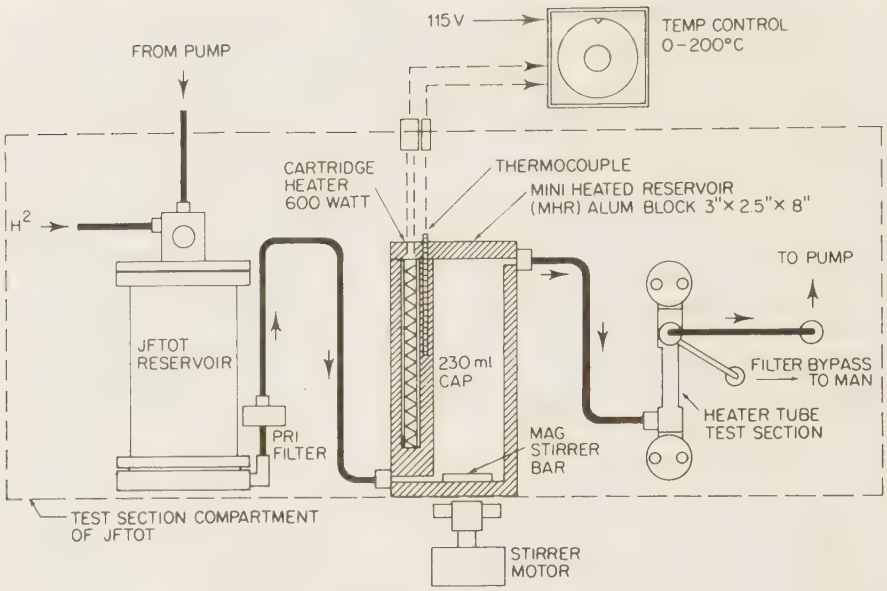

FIG. 14. Flow schematic of JFTOT test section compartment with integral MINI HEATED RESERVOIR (MHR).

Yet another technique being developed for research is to use the JFTOT, with and without MHR, and rate the tube by a carbon burn-off technique. For this technique the tube must be scrupulously cleaned prior to use, handled very carefully in the JFTOT and then placed in a furnace in a stream of clean air to burn off the carbonaceous deposit. As the tube is aluminium the furnace temperature must be such that it does not melt the tube. The products of combustion are then passed through a packed hot furnace to complete oxidation to CO_2 and water. The water is removed in a silica gel tower and the stream enters an infra-red CO_2 analyser. From this total deposit can be calculated in micrograms. This technique has significant possibilities in the evaluation of fuels for the future.

Fuels of higher thermal stability than are required in typical specifications can be produced by various refinery processes. They are more complex fuels and have a more restrictive specification; consequently they are costly and are not produced in large quantities.

In the British aviation turbo-fuel specifications (DERD) the use of an anti-oxidant is mandatory in the fuels which have been hydrogen treated to prevent gum formation and peroxidation after manufacture. Also the use of a metal deactivator is optional. Both these additives tend to improve thermal stability, although this is not the prime reason for their use.

Combustion quality

Combustion in a jet engine converts the energy, in the form of a liquid fuel, into useful work and this of course is the prime function of the fuel. Considerable research and development effort has, therefore, been devoted to the production

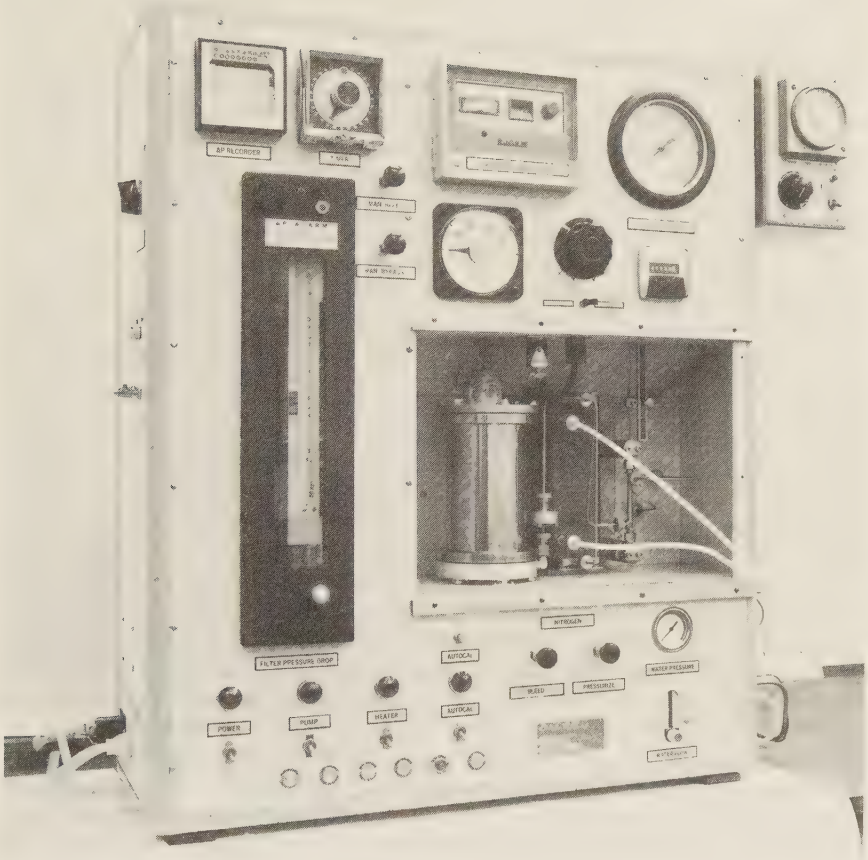

FIG. 15. JFTOT rig with MHR incorporated.

of fuels with good combustion qualities, and also to the production of effective specifications to control these qualities. The quality of combustion is dependent on the carbon/hydrogen ratio of the fuel (fixed by crude source and type of processing) and the flame speed. The flame speed is also a function of fuel composition, as well as temperature and oxygen concentration. So, for good combustion, fuel type is important, and must be specified and controlled. For ideal burning conditions the lowest carbon/hydrogen ratio possible is required—this would mean an entirely paraffinic fuel. Such a fuel could be produced, but would be restricted in volume and prohibitive on cost, as crude oil not only contains a wide variety of components but the distribution of these components varies considerably with the crude source. As a result, fuel specifications are written so as to be a reasonable compromise between what is ideal and what is available. In the gas turbine combustion system the aromatic compounds are the most difficult to burn and can result in the production of carbon, which forms smoke, and hence does not release all of its available energy. They also emit a high radiant heat from a luminous flame. For this

reason turbo-fuel specifications contain a maximum aromatics content. Combustion chambers are designed to operate efficiently with this percentage of aromatics present in the fuel.

A more direct control on combustion is imposed by a smoke point specification (IP Method 57). The smoke point is the maximum flame height, in millimetres, at which a fuel can be burnt in a standard wick-fed lamp without smoking. On turbo-fuel from Middle East crudes a smoke point minimum and aromatics maximum provide sufficient combustion control. However, on some Western Hemisphere crudes the smoke point does not give a good correlation with engine performance. The polynuclear aromatics (naphthalene content) of a fuel, as determined by u.v. absorption at a wavelength of 285 mμ (ASTM D 1840), gives a reasonable prediction of combustion performance and is less restrictive than a 25 mm smoke point. This test is therefore specified as an alternative test to smoke point in some specifications, with an upper limit of 3 per cent.

Another test method has been devised which actually measures the emissivity of the flame and so is a direct control of the radiant heat in the primary zone of the combustion chamber. Too high a radiant heat will reduce the life of the flame tube, and so must be avoided. The apparatus for this test is a luminometer, and the fuel under test is rated on an arbitrary scale known as the luminometer number of the fuel. A high number denotes a fuel of good combustion quality. In British specifications a smoke point of 20 mm minimum and naphthalene content 3 per cent vol maximum, plus a total aromatics limit of 22 per cent vol maximum, give adequate control. In some specifications, however, the luminometer number is specified as an alternative to smoke point (e.g. ASTM Jet A-1 and IATA Guidance Material for kerosine).

It was stated at the beginning of this section that combustion quality is dependent on the carbon/hydrogen ratio of the fuel. So the most obvious control would be to know this ratio. Unfortunately, until a few years ago, apart from complex combustion techniques, there was no easy way of determining the hydrogen or carbon content of the fuel. Then a most effective technique was discovered to measure the hydrogen content of a liquid hydrocarbon with great precision. The technique was to use low resolution nuclear magnetic resonance (NMR). The Newport Analyser Mark III, manufactured by Oxford Instruments, is such an instrument. It has been fully evaluated by the IP and ASTM, and the method is published as IP 338/ASTM D 3701. Accurately knowing the hydrogen content the carbon/hydrogen ratio may easily and accurately be determined, and hence the combustion characteristics of the fuel accurately known. It was hoped that hydrogen content would go into turbo-fuel specifications as the prime combustion parameter, and that with time the present combustion parameters of aromatics, olefins, smoke point withdrawn. In anticipation of this the DERD 2494 specification already allows that if one has a high hydrogen content fuel, 13.8 per cent mass or greater, then the determination of olefins, specific energy, aniline-gravity product, smoke point, and naphthalenes is waived.

Unfortunately in the United States an engine manufacturer has challenged the ASTM that he cannot correlate hydrogen content with jet engine combustor life but with the current parameters he can. A committee of the CRC has been formed to resolve this problem, and until the findings are known

no further progress can be made on the introduction of hydrogen content into international turbo-fuel specifications as a control of combustion quality.

If one assumes that they find in favour of hydrogen content giving adequate information, then with the changing scene world-wide in crude availability it is reasonable to assume changes in turbo-fuel composition within the next 15 to 20 years. With this in mind the likely outcome is to define a turbo-fuel with a minimum hydrogen content and another parameter to limit higher aromatics, that is 2- or 3-ring aromatic compounds, such as naphthalene content. When this approach is agreed upon it will be possible to delete aromatic content, olefin content, and smoke point/luminometer number from specifications.

For the wide-cut type of turbo-fuel the best correlation with combustion chamber deposits is derived from a function of smoke point and fuel volatility known as the Smoke Volatility Index (SVI). It is defined as:

SVI = smoke point + 0.42 (per cent of fuel boiling below 400 °F as measured in the standard distillation test) (IP 123/ASTM D 86)

Again with the introduction of a hydrogen content into the fuel specification this parameter could be deleted.

Specific energy

The change in specific energy, formerly known as calorific value, on a weight basis occurs within fairly narrow limits. In practice it is difficult to make much use of this by the complexity of obtaining fuels of suitable composition. The possibilities of increasing the specific energy on a volume basis are less restrictive and this fact was discussed and illustrated under density.

Aviation turbo-fuel specifications set minimum values for the net (or lower) specific energy per unit weight, so that combustion engineers have a value for their design case. As illustrated when discussing density, as the density increases the specific energy on a weight basis decreases. But as the density increases the specific energy per unit volume increases. For maximum energy, therefore, in a volume-limited situation, a high density fuel is required—the penalty is, however, increased weight.

Table X illustrates the effect of increasing density on the net specific energy, both by weight and volume on specific fuels. Figure 7, net specific energy versus density, has shown the general case.

TABLE X

Typical Specific Energy Values for Aviation Turbo-fuels

		Net specific energy	
Turbine fuel	Density at 15 °C	Mass (kJ/kg)	Volume (MJ/m^3)
Wide-cut	0.755	43 613	32 839
Kerosine type	0.795	43 380	34 232
High-flash kerosine	0.824	43 007	35 369

Storage and Handling Problems

Procedures for storage, handling, and into-plane refuelling of aviation turbo-fuel in the UK are laid down by the Air Registration Board and the Materials Quality Assurance Directorate of the Ministry of Defence. These regulations, supplemented by oil company regulations and various contract agreements between purchaser and supplier, ensure that clean, dry fuel is supplied into aircraft from refuellers or hydrant systems. The handling procedures include the safety aspect to protect both personnel and equipment from a fire or explosion hazard.

Turbo-fuel cleanliness

Particulate matter and free water have always been undesirable contaminants in aviation turbo-fuels. Although the volume of fuel used by gas turbine engines is steadily increasing the total amount of contaminant in the fuel is steadily decreasing, on a unit volume basis. A quality requirement for a fuel ex-refinery is clear and bright and free from suspended matter, but on its journey to the aircraft the fuel may travel by sea-going tanker, rail-car, or pipeline, and is liable to pick up dirt, finely divided rust and/or free water. The increasing use of surfactant type additives (anti-static additives and corrosion inhibitors) is not helping the problem.

To ensure that the fuel is cleaned up at the time of delivery into aircraft, filter separators are used in the distribution system. Filter separators, as the name implies, remove solid particulate matter by filtration and separate out the free water by a coalescing action. The specification test used by a number of organizations for filter separator element approval is the US military Mil-F-8901A specification. This is designed to reduce free water to acceptable levels (<30 ppm) and to reduce the dirt level to <1 mg/l fuel. The approval test against this specification is to contaminate a fuel with 37.8 mg/l (172 mg/UK gal) of a fine iron oxide powder, and to check that the filtered product contains <1 mg/l particulate matter. Most aviation turbo-fuel specifications stipulate the maximum dirt content allowed into plane and this is of the order of 1 mg/l of fuel. As a control on the dirt content of the fuel, samples are taken from the loading line during refuelling. At the end of the refuelling hose, where it is attached to the aircraft, is a sample point. From this a known volume of fuel is passed through a pre-weighed cellulose membrane filter (0.8 μ porosity), the filter dried of all liquid fuel, and reweighed. From this the dirt content of the fuel on a volume basis may be determined.

The most generally accepted system of measuring particulate contamination is supplied by the Millpore Filter Corporation.

The fuel velocities involved in modern transport systems, large tankers, and pipelines, tend to promote the dislodging of fine scale from the system, and hence a practice has developed of allowing the fuel to settle for a given time in product tankage to allow the scale to fall to the bottom of the tank. It has been the practice to allow a turbo-fuel to settle for 1 hr/ft depth of stored fuel; in this way it was considered that all the particulate matter would settle to the bottom of the tank. World surveys have shown that in airfield tankage there were strong indications that the dirt level of turbine fuels was not being reduced

significantly by the settling periods imposed. This appears to be because fuel systems are much cleaner than they used to be, and most of the contaminant present is very fine material which tends to be held in suspension almost indefinitely and requires micro-filtration for effective removal.

Long settling times are, therefore, unnecessary, tie up tankage, and impose throughput restrictions on depots. Microfiltration of the product from the tank is carried out, however, and the product is removed from the tank by means of floating suction, that is the product is taken from the tank via a pipe floating some 1 metre below the surface of the liquid.

Static electricity. Owing to the high state of cleanliness and the purity of the product, a typical aviation kerosine has a conductivity of about 1 picosiemen/metre, known as a conductivity unit (CU). For comparison, demineralized water has a conductivity of 10 000 000 CU. Thus aviation turbofuel has a very low conductivity. The conductivity of the fuel affects the rate at which the charged ions are removed from the fuel, that is the charge relaxation. The time taken for the charge in the fuel to fall from a given value to half that value (the fuel's half-value time $= t_{1/2}$) is an important factor, and gives an indication of whether static charges are likely to be a hazard or not. In practical units:

$$t_{1/2} = \frac{12}{\text{conductivity (CU)}} \text{ sec}$$

Typical values of conductivity:

Aviation kerosine 1 CU; $t_{1/2} = 12$ sec
Demineralized water 10^7 CU; $t_{1/2} = 48\ \mu$sec
(dielectric constant for hydrocarbons ≈ 2
for water $= 80$).

Charges can accumulate to an appreciable extent only if the relaxation time and the half-value time are high.

How are these charges formed? Let us consider a pipeline system where with no flow a charge transfer takes place across the fuel/pipe interface and a resulting double layer of charge is established. This is illustrated in Fig. 16(A). Under flow conditions (Fig. 16(B)) the positive charge in the fuel is carried downstream and the negative charge on the pipe is now free to flow harmlessly to earth. In a pipeline system, we have, therefore, a continuous process of contact and separation of fuel with the pipe wall and a gradual build up of charge on the fuel.

Fig. 17 shows how charge separation occurs in a filter. As static generation is a surface phenomenon, and micronic filters have very large surface areas exposed to the fuel, high charge separation rates result. Flow through filters and filter separators causes charge densities much higher than those obtained from flow in a pipe.

Because of the low conductivity of the fuel charged particles take a considerable time to dissipate or relax. Increasing velocity will increase the charge in the fuel, and flow through a filter will by itself generate a considerable charge in the fuel. Equivalent charges will be generated in the pipelines and filter elements, but as the equipment is usually made of metal, a conducting

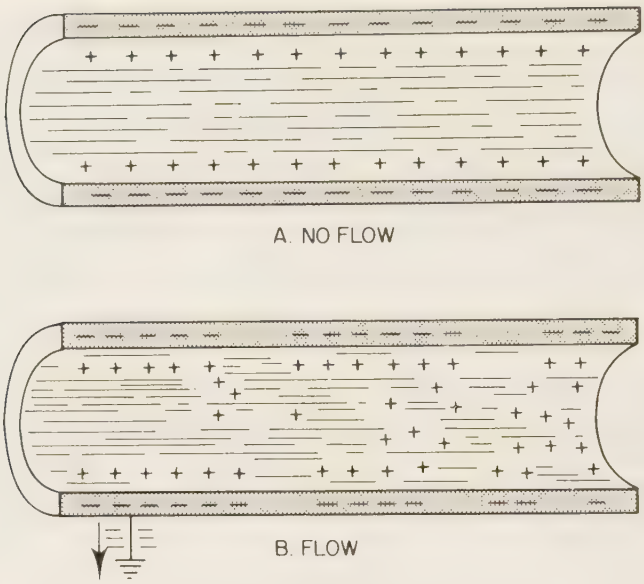

FIG. 16. Charge separation in pipe.

material, it will be earthed and so the charges will not accumulate on the equipment but leak away to earth.

In a fuel transfer system it is most important that all parts of the system are adequately electrically bonded, that is that all the parts are at the same potential, and preferably that the system is earthed.

The generation of static electrical charges in the handling of aviation turbofuels has long been recognized as a potential safety hazard. A number of rules covering pumping rates, line velocities, bottom loading (no splash filling), and settling times have been generally adopted by the major oil companies as standard practice for the safe handling of these products. The success of these practices may be measured by the fact that there have been no reported incidents of fire or explosion which have been positively attributed to the generation of static electricity during the underwing refuelling of commercial jet aircraft.

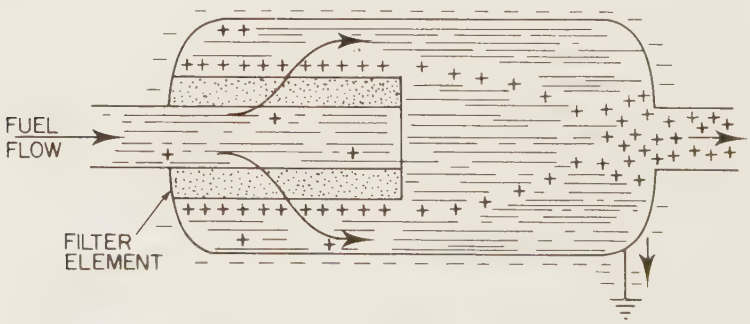

FIG. 17. Charge separation in filter.

As an additional safety precaution an anti-static additive, or more correctly, a static dissipator additive, may be added to aviation turbo-fuels. The additive permitted for use in DERD 2494 specification is called ASA-3, and its addition rate to the fuel is 1 ppm maximum. The conductivity limits, at the point, time and temperature of delivery to the purchaser, are 50 to 450 pS/m. The amount of additive required depends upon the crude source from which the fuel was produced, since varying the detailed chemical composition of the fuel affects the additive response. Another static dissipator additive, Stadis 450, is undergoing evaluation by aero-engine manufacturers, airframe manufacturers, and fuel system component manufacturers. It appears that all of these approve of the use of this additive, and formal approval of its use in international specifications is expected soon. It is anticipated that its addition rate for the same fuel conductivity will be twice that specified for ASA-3.

The conductivity of a fuel in a tank may be measured directly by portable meters manufactured by Maihak or Emcee Electronics Inc. In the case of the Maihak instrument it has a conductivity cell on the end of a cable wound onto a drum. The cell is lowered, on the end of the cable, into the tank through the sampling hatch, and the direct reading meter is attached to the drum. With the Emcee instrument, which may be carried in the pocket, the conductivity cell may be attached directly to it and the instrument put into fuel in a sample container or the cell may be attached to the end of a probe and inserted into a tank. In both cases a direct reading may be read off the instrument.

It is usual to dilute a static dissipator additive with fuel before making an addition to bulk fuel. This is done to ensure adequate dispersion of the additive in the fuel.

At the concentration used static dissipator additives have no effect on the thermal stability or oxidative stability of the fuel or on its combustion quality. Owing to the surfactants present in the additives the Water Separometer Index (modified) (WSIM) of the fuel may be reduced by some 5 points. With fuel of borderline quality this reduction could be 10–15 points.

All major airport fuel systems are required to use filter/separator elements which have been qualified in dirt and water tests with fuel containing ASA-3, and so the initial effect that some elements could be adversely affected by fuel containing ASA-3 has been eliminated. All major airport refuelling systems make every effort to keep these systems clean and dry, and regularly monitor their system. New methods are currently being evaluated to ensure that filter/separators operate properly, including an on-line system to check that the filter/separator is coalescing.

BOOST FLUIDS

In order to obtain extra power or thrust for a short time, generally for take-off, water or water/methanol blends may be injected into the engine. The object of this injection is to keep the temperature of the gases entering the turbine section of the engine constant and not above a given maximum. If no other action were taken the temperature of the gases leaving the combustion chamber, that is entering the turbine section, would rise and damage the turbine blades. Sufficient water or water/methanol must be added to adsorb this extra heat, as latent heat of vaporization, and so keep the temperature in the turbine section

controlled. As thrust is proportional to mass, the extra mass flowing from the combustion chamber will give the required extra thrust.

Water or water/methanol is also used to restore power which would otherwise be lost owing to high ambient air temperatures. As the ambient temperature rises the same volume of intake air has less mass. If this air can be cooled down the original mass flow may be restored, and hence the original thrust achieved.

In order to protect the turbine blades and metering systems, both the water and the water/methanol mix must be of a high purity. Demineralized water is always specified for this purpose. Methanol can attack sealants used in some aircraft systems, but has a lower freezing point than water. These two factors influence the use of either water alone or a water/methanol mixture for a boost fluid. The quality of these fluids is laid down in DERD 2491, which incorporates BS 506 for methanol.

Water injection can have the effect of either considerably increasing exhaust smoke or drastically reducing it, depending on the manner in which it is injected into the combustion chamber. Smoke emission from combustion systems is receiving very considerable attention world-wide as part of air pollution control.

The amount of smoke emitted from gas turbine engines depends essentially on combustion chamber design, and the present turbine fuel specifications control the fuel within reasonable limits. New engines are designed with very low smoke emission levels, and in fact do not even need to use boost fluids either for the extra power for take-off or to control smoke emission on take-off.

THE FUTURE

The 1970s saw the end of the gasoline-fuelled piston-engined aircraft for large civil aircraft, the introduction of the world's first supersonic transport aircraft and the introduction, on a large scale, of wide-bodied large-volume subsonic aircraft. It also saw the fuel crisis in 1973. This has drastically affected aircraft design and operation. Aircraft fuel costs have risen dramatically and fuel volumes have increased faster than the volumes of other products from crude oil. Total crude available has been less than predicted and fuel conservation has become of prime importance.

Aviation kerosine is now the major fuel used on all civil jet aircraft, and several countries also use it in their military aircraft as well. This means that little wide-cut fuel is used and very large volumes of kerosine type fuel used. This led to a shortage of fuel and allocation to airlines in the late 1970s. The raising of the freezing point of the fuel from $-50\,^{\circ}C$ to $-47\,^{\circ}C$ gave an increase in the volume available, and so the fuel is no longer in short supply.

For the future, however, it is predicted that fuel specifications may have to get broader or more relaxed if the volumes required are to be obtained. A lot of research work on the type of fuel that will be required, and the effect this will have on current and future engines, fuel systems, and airframes, is being carried out by NASA and the major engine and aircraft manufacturers. NATO/AGARD has had a working group studying the problem, and as a consequence has set up another working group to predict the type of fuel which will be available in the future.

Safety fuels based on emulsions and gels for military purposes never developed to successful production, but there is a very considerable interest, both in the USA and UK, in the development and production of an anti-misting kerosine.

In the 1973 edition of this book predictions were made for second-generation supersonic transports (Mach 3.0) and even hypersonic aircraft (Mach 5.0+). In the present situation these are out, both for development and operating costs. The trend is now for energy-efficient engines and aerodynamic designs for maximum lift and minimum drag for long-range large aircraft and medium-sized short-haul aircraft, so that the operating cost per seat–kilometre is kept down. With all this the fuel for the future will be a kerosine type modified only so much that there will be the volume available to meet requirements and still maintain the quality required for safe operation.

20

Fuels for Spark-ignition Engines

By K. OWEN

1 INTRODUCTION

In the early days of the automobile at the end of the 19th century the only suitable fuels available were coal tar distillates and the lighter fractions from the distillation of crude oil. Since then great steps have been made in the development of fuels and these have enabled engine designers to improve dramatically the performance of their vehicles. The general use of lead alkyls from the middle of the 1920s, the development of processes for making high-octane blending components and the widespread use of additives which enhance many quality aspects have all contributed to the highly developed gasolines we use today.

The primary requirement of a gasoline is that it should burn smoothly, without exploding, under the conditions existing in the combustion chamber of a spark-ignition engine, so that the maximum amount of useful energy is liberated. There are, however, several other properties that are essential for the proper performance of the engine. Thus the volatility must be such that when the gasoline is mixed with air in the carburettor it readily forms a combustible mixture; on the other hand, it must not evaporate so easily that losses from the tank are excessive or that boiling occurs in the fuel system. It must not allow undue formation of ice in the carburettor, nor must it give rise to excessive deposits in the combustion chamber. There must be no attack on the various engine components with which it comes into contact, nor must the fuel deposit gum or other material likely to block orifices or cause sticking of valves. The final marketed product must satisfy a number of criteria, all of which can be assessed by recognized standard tests.

2 GASOLINE MANUFACTURE AND COMPOSITION

Motor gasoline has, until recent years, consisted almost entirely of a complex mixture of hydrocarbons derived from crude oil and boiling between about 30°C and 220°C, i.e. containing compounds in the range C_4 to C_{12}. Today, in some gasolines and in some countries, alcohols and other oxygenated compounds are also used as blending components or even as motor fuels in their own right, and these are discussed in Sections 11 and 12. Small amounts of additives are usually incorporated in order to enhance various performance aspects of the fuel, and are also discussed later (Section 8).

Historically motor gasolines have been classified according to their octane (or anti-knock) quality and in the UK a star system is used in which 2 star is 'Regular' and 5 star (no longer available) is 'Super premium'. Gasolines can vary widely in composition even if they are of the same grade (star rating). This is because refineries differ in the range of products they supply and so differ in

TABLE I

Main Components of Gasoline

	Component	Process	Boiling range °C	Research ON at		Sensitivity	Remarks
				Zero lead	0.15 g/l Pb (TEL		
I	Paraffinic						
	Butane	Crude oil distillation Conversion processes	0	94–97	96–100	<5	Widely used in proportions up to 15%. High-octane, high vapour pressure component.
	Isopentane	Crude oil distillation Conversion processes Isomerization of *n*-pentane	27	94–96	98–100	<5	Widely used as high-octane, high volatility component.
	Alkylate	Alkylation process	40–150	90–100	93–105	<5	Mainly used in premium fuels to improve the motor octane quality.
	Isomerate	Isomerization of nC_5 and nC_6 hydrocarbons	40–170	85–90	88–93	<5	
	Straight-run naphtha	Crude oil distillation	30–200*	50–70	65–85	<5	Widely used low-octane component.
	Hydrocrackate	Hydrocracking process	40–200*	75–85	80–90	<5	Contains also aromatics. Some fractions may be used as feed for catalytic reforming.
II	Olefinic						
	Thermally cracked naphtha	Thermal cracking of heavy distillate	40–200	75–85	80–90	10–15	Obsolescent process.
	Catalytically cracked naphtha	Catalytic cracking of heavy distillate	40–200*	85–95	90–98	10–15	Widely used component. Light cat napthas in regular grades.
	Visbreaker naphtha	Visbreaking of fuel oil	40–200*	75–85	80–90	10–15	Used mainly in premium gasoline. Contain also aromatics.
	Steam cracked naphtha	Steam cracking	40–150	85–95	90–100	10–15	By-product of chemical process. Contains also aromatics.
	Polymer	Polymerization of light olefins	60–200	92–97	95–98		High-octane component but not widely used.
	Coker naphtha	Coking (cracking to give coke)	40–200*	85–95	90–98	10–15	Becoming more important due to need to minimize fuel oil production.
III	Aromatic						
	Catalytic reformate	Catalytic reforming	40–200*	85–95	90–105	5–10	Most widely used high-octane component of gasolines.

* Often fractionated into light and heavy products.

the processes that they have available. Each refiner has to select the processes that will best enable him to meet the quality and volume of all the required products at minimum cost.

The hydrocarbons which make up the bulk of a gasoline are normally categorized into three general types: paraffins, olefins, and aromatics. Table I summarizes the most important gasoline component streams as manufactured by processes described in preceding chapters, and shows to which of the above hydrocarbon types they belong. Many of the streams do not contain hydrocarbons exclusively of one type, e.g. steam-cracked naphthas and catalytically-cracked naphthas contain compounds from all three categories. In these cases any component that contains olefins is classified as olefinic, otherwise the most important compounds present are used for classification.

A motor gasoline must have an odour that is acceptable to consumers and so must be essentially free of any constituent that has an unpleasant smell. Thiols come into this category and are removed by refining processes before blending.

3 THE SPARK-IGNITION ENGINE

Before discussing in detail the characteristics of a gasoline that are important in ensuring the correct performance of an engine, a brief account is given below of these aspects of the spark-ignition engine that are of most concern to the gasoline technologist. This has been done by following the flow of the fuel from the tank to the emission of the combustion products from the exhaust.

Gasoline is pumped from the tank and delivered to the carburettor. This is a device, operated by engine suction, having as its primary function the metering of liquid fuel and air in the required ratio for any given engine operating condition. A secondary function is to atomize the fuel so as to achieve adequate homogeneity of the air/fuel mixture. The amount of mixture is controlled by a butterfly valve or throttle operated by the accelerator pedal. The fuel/air mixture can be enriched for cold starting by various means depending on the carburettor type. The use of fuel injection systems instead of carburettors is becoming more common, in spite of being more expensive, since they do allow a much closer control of the fuel/air mixture. This can give, particularly when used with microprocessors and feed-back controls, improved economy, more power, and lower undesirable exhaust emissions.

The fuel/air mixture passes into the inlet manifold where, usually with the aid of some form of heating, vaporization of the fuel is completed. The charge is then delivered to the combustion chambers by way of the inlet valves, compressed by the pistons and fired by the spark plugs. The pressure developed by the combustion process must be smooth and controlled in order to make maximum use of the energy liberated. The fuel factors that influence this will be discussed in some detail (Section 5). However, engine factors also play an important part, such as the shape of the combustion chamber, the degree of compression of the charge, the level of engine cooling, the timing of the spark, and so on.

After combustion, the hot gases are exhausted from the cylinders via the valves through the exhaust and silencer system, and are finally emitted into the atmosphere.

During this whole process, both the physical and the chemical properties of the fuel play important parts.

4 FUEL PHYSICAL CHARACTERISTICS INFLUENCING CARBURATION

The physical characteristics of a fuel that can influence carburation, other than volatility which is discussed in detail later, are specific gravity, viscosity and surface tension.[1] They all affect the air/fuel ratio of the mixture and hence can have an indirect effect on fuel economy and exhaust emissions, as will be discussed later.

When considering the flow of fuel through a carburettor jet, the coefficient of discharge (C) for normal hydrocarbon fuels is virtually constant above a critical value of the Reynolds number. Under these conditions the mass flow is a direct function of d, where d is the specific gravity of the fuel. Thus increasing specific gravity increases the mass flow and therefore increases also the fuel/air ratio of the mixture. This is partly offset by the lower level in the float chamber that occurs with heavier fuels.

With regard to viscosity, the coefficient of discharge (C) is a direct function of the Reynolds number which itself is an inverse function of the fuel viscosity. However, since C is constant above a critical value of the Reynolds number and since also for most cars the Reynolds number is always above this critical value, normal variations in fuel viscosity have little influence on flow. When fuels have viscosities above the normal range, however, as for example when thickening agents are used,[2] the Reynolds number may fall below the critical value so that non-turbulent flow occurs. Under these circumstances increasing viscosity will decrease fuel flow beyond the design level and the fuel/air ratio of the mixture will decrease.

Surface tension also influences flow through jets, since increased venturi suction is required to overcome the surface tension at the discharge nozzle. Increasing surface tension will reduce mass flow and so will reduce fuel/air ratios.

As fuel temperature increases, specific gravity, viscosity, and surface tension decrease. For most conventional carburettors operating in the low-load range, as might be expected from the above, the mixture becomes richer as fuel temperature is decreased. This effect is at a maximum at idle.

It is not possible to give more than simple directional influences as the above physical fuel factors change since it has been found that different carburettor designs and engine operating conditions give rise to varying degrees of enrichment or leaning with changes in these fuel properties.

5 COMBUSTION OF GASOLINE

5.1 The Combustion Process

In a spark-ignition engine the mixture of fuel and air aspirated into the cylinder is compressed and then ignited by a spark. Combustion proceeds by means of a flame front moving through the mixture in a rather irregular fashion because of turbulence and incomplete mixing until, in an ideal situation, all of

the fuel has been converted into carbon doxide and water. In the practical case, however, some of the hydrocarbons are unburnt or incompletely burnt, carbon monoxide is formed as well as carbon dioxide, and to a small extent some of the nitrogen and oxygen from the air combine together under the temperature conditions in the combustion chamber to form oxides of nitrogen. These unburnt hydrocarbons, carbon monoxide and oxides of nitrogen are undesirable constituents of exhaust gas because of their contribution to atmospheric pollution.

Oxidation of the fuel is a complex process. Before the charge is consumed by the flame the combustion process has already started in a series of 'pre-flame' reactions. It depends on the extent of these pre-flame reactions whether or not the smooth burning that allows maximum power to be obtained from the engine is achieved.

Different hydrocarbons show marked variations in their pre-flame and ignition characteristics, and so differ in their combustion behaviour in an engine. The use of additives such as lead alkyls can inhibit pre-flame activity and is discussed later. First let us look at the influence of the other variables that influence combustion and efficiency in an engine. The most important of these are air/fuel ratio, the extent to which the air/fuel mixture is compressed before ignition, and the timing and energy of the spark.

5.2 Air/Fuel Ratio

The amount of air required to oxidize a hydrocarbon fuel completely to carbon dioxide and water can readily be calculated. For example, heptane under perfect combustion conditions is oxidized as follows:

$$C_7H_{16} + 11O_2 = 7CO_2 + 8H_2O$$

In this case 1 volume of heptane requires 11 volumes of oxygen or 52.6 volumes of air. On a weight basis this is equivalent to an air/fuel ratio of 15:1. For gasoline one part by weight requires about 14.5 parts by weight of air, although the exact stoichiometric amount of air will depend on the precise hydrocarbon composition of the fuel. Generally speaking, if the air/fuel ratio exceeds about 20:1 then the mixture will be too weak to ignite at all, and if it is less than about 7:1 it will be too rich. Again each hydrocarbon has its own flammability limits so that the range of flammability of a fuel will also depend on its exact hydrocarbon composition.

The stoichiometric air/fuel ratio is not the one which gives the maximum power or maximum thermal efficiency, as is shown in Fig. 1.

Thus, when maximum power is needed, as for example under full throttle conditions, a rich mixture is preferred. For normal cruising the most economic mixture is one that is weaker than stoichiometric to maximize thermal efficiency. It is clearly important that the carburettor should be able to provide as far as possible the correct mixture for all operating conditions.

In recent years a number of lean burn, homogeneously charged engines have been described which allow the use of air/fuel ratios well beyond those possible with the conventional engines considered in the discussion above. Such engines also have high compression ratios (in the range 11 to 14) and so have excellent fuel economy. The thermal efficiency reaches a maximum at around 20:1

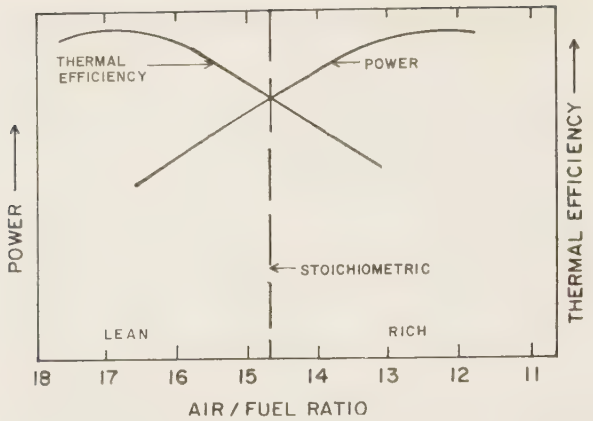

FIG. 1. Influence of air/fuel ratio on power and thermal efficiency.

air/fuel ratio but with some sacrifice of engine peak power. Beyond this level performance deteriorates due to air increase in misfire as the flammability limit of gasoline is approached. However, the use of these engines is very limited at present (1983), but is likely to increase as further development takes place.

Carburation problems unfortunately do not stop at the carburettor. The inlet manifold design plays a large part in ensuring that each cylinder in a multi-cylinder engine receives the correct air/fuel ratio. Mal-distribution of fuel in the inlet manifold can result in some cylinders receiving a leaner charge than others, and this will upset the efficiency of the engine. Segregation of fuel components in the manifold so that some cylinders receive lower octane components than others can also occur during acceleration. (See Section 5.5.)

Air/fuel ratio and exhaust emissions

Air/fuel ratio has a considerable effect on the emission of undesirable combustion products from a spark-ignition engine, and the pressures to reduce air pollution have led to many vehicles being designed to run at lean air/fuel ratios. This has the effect of reducing carbon monoxide and hydrocarbon emissions and of increasing nitrogen oxides as shown in Fig. 2.

In this particular engine some misfiring would occur above 16:1 air/fuel ratio which would result in an increase in hydrocarbon emissions. Nitrogen oxides arise from the oxidation of atmospheric nitrogen in the cylinder, and the amount formed depends on flame temperature and availability of oxygen. Generally speaking, in Europe, nitrogen oxides and hydrocarbons are less of a problem than in, for example, California, USA, since the conditions do not occur so frequently for the formation of 'photochemical' smog. This is found only when there is a high concentration of nitrogen oxides and hydrocarbons in the atmosphere on sunny, windless days, particularly during temperature inversion conditions.

Carbon monoxide is not a factor in causing photochemical smog, but it is of concern because of its toxicity. Unburnt and partially burnt hydrocarbons are also regarded as undesirable, mainly because of their unpleasant odour. Poly-aromatic hydrocarbons (PAH), sometimes called poly-cyclic aromatics, are of

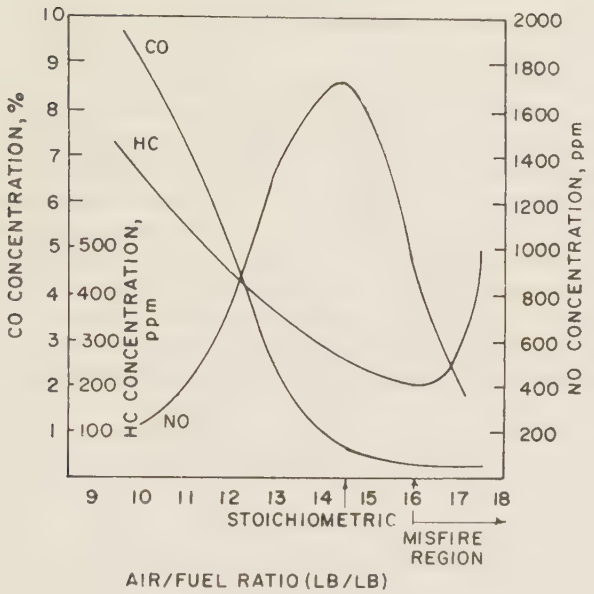

FIG. 2. The effect of air/fuel ratio on HC, CO, NO_x emissions (1.3-1 engine, 3000 r.p.m., road load).

concern because of the carcinogenic properties of certain members of this chemical type.

Fuel parameters have little influence on exhaust emissions, although additives which keep the combustion chamber and inlet systems clean and free from deposits play a small part. Fuel volatility also has some influence because of its effect on evaporation losses, warm-up, and carburation. The most effective methods of emission control are mechanical modifications to the engine. For reduction of CO and hydrocarbons, new combustion chamber designs allow operation at leaner air/fuel ratios, and there are devices to give further oxidation in the exhaust manifold. Improved carburettors and inlet manifolds ensure more complete air/fuel mixing, and together with fuel injection systems, modifications to ignition timing, reduced valve overlap (i.e. the period when both exhaust and inlet valves are open together), etc. help to minimize these emissions. Reduction of nitrogen oxides in the exhaust involves either a drop in flame temperature, e.g. by recycle of some exhaust gases, or running with a richer mixture and the use of catalysts.

In general it can be said that regulations introduced over the past ten years have resulted in very considerable improvements being made to the exhaust emissions from spark-ignition engines, but often at the expense of fuel economy.

5.3 Influence of Compression Ratios on Combustion

The relationship between the compression ratio and the efficiency of an internal combustion engine is well covered in many textbooks on engines.[3,4] In brief it can be shown that the theoretical thermodynamic efficiency of an

engine increases with increasing compression ratio according to the relationship

$$E = 1 - (1/r)^{\gamma - 1}$$

where E is the efficiency, r is the compression ratio, and γ is the ratio of the specific heats at constant pressure and constant volume of the working fluid. This theoretical equation assumes that air is the working fluid, that it is a perfect gas, that there are no heat losses, etc. In practice, by replacing γ with an experimentally determined figure, an acceptable relationship of thermal efficiency to compression ratio is obtained. The actual level of thermal efficiency and the influence of compression ratio will vary from engine to engine, but Fig. 3 shows a fairly typical curve of the effect obtained when compression ratios are changed in a conventional engine.

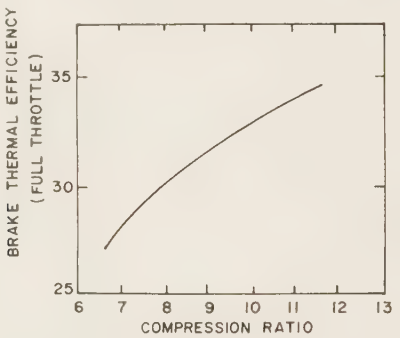

Fig. 3. Effect of compression ratio on brake thermal efficiency.

An improvement in thermal efficiency gives rise, of course, either to more power for the same size engine or to improved fuel economy at the same power output. There are indications that thermal efficiency reaches a maximum at a compression ratio of about 17:1.[5]

5.4 Influence of Ignition Timing on Combustion

The compressed charge of air and fuel in the cylinder is ignited by means of a spark. The minimum amount of energy required for ignition depends on the mixture strength, the spark gap and the cylinder pressure, but normally the energy available is very much greater than is actually necessary.

In order to get optimum efficiency the spark should occur at the right time in the cycle, so that maximum pressure by the burning of the charge is achieved about 15 or 20° after the piston has reached top dead centre. The actual timing of the spark to achieve this will depend on the speed of the engine, and ignition systems are built to obtain the best timing under all running conditions. Small deviations of a few degrees from the best position are not usually important in affecting power output, and this is fortunate since slackness and wear in the distributor together with mechanical mal-adjustments, mean that a considerable proportion of cars on the road are not at their optimum ignition timing. However, spark-ignition variations can also give rise to abnormal combustion

problems such as knock (see Section 5.5), and this is usually more important than the influence on power output.

Ignition problems can arise from a number of causes. Oxidation of the points in the distributor can cause misfire, as can deposits on the spark plug gap. Ignition can sometimes occur at the wrong time relative to the engine cycle because of hot or glowing surfaces. These abnormal combustion phenomena will be discussed in Section 5.7.

5.5 Knock

Knock or detonation occurs when the unburnt gases ahead of the flame front spontaneously ignite, giving rise to an excessive rate of pressure rise, thereby causing the characteristic knocking or 'pinking' sound. Under knocking conditions, ignition of the mixture and the initial burning process proceed quite normally, but the 'end gas', i.e. that part of the unburnt charge ahead of the flame front, is compressed and heated by the advancing flame front until it reaches the point of self-ignition.

Studies of the pre-flame reactions taking place in the cylinder indicate in general that those fuels which undergo the greatest amount of pre-flame oxidation have the greatest tendency to self-ignite, and are therefore the most susceptible to knock.

The problem of knock is important in spark-ignition engines for a number of reasons. First, it represents a design limitation in achieving maximum power output and efficiency. Secondly, it can cause or contribute to engine damage under severe conditions and lastly, the disturbing noise it makes can cause apprehension on the part of the motorist.

Measurement of anti-knock quality of a gasoline

The anti-knock quality of a gasoline is measured using a purely arbitrary scale of octane numbers suggested by Graham Edgar in 1926. In this scale iso-octane is given a value of 100 and *n*-heptane a value of zero. The octane number of the fuel is the percentage of iso-octane in a blend with *n*-heptane that has the same anti-knock performance under standard test conditions as the fuel under test. For octane values above 100, mixtures of iso-octane and tetraethyl lead are used as the standard.

Single-cylinder variable compression ratio engines, known as CFR engines, are used for knock rating, and were first accepted for this purpose by the Cooperative Fuel Research Council in the USA in 1930. Briefly the procedure followed is to vary the compression ratio to obtain a standard knock intensity as measured by an electronically controlled knock meter, using an air/fuel ratio that gives maximum knock. When this knock meter reading is bracketed by two reference fuels (made from iso-octane and *n*-heptane) differing by two octane numbers, the rating of the sample is calculated by interpolation.

Over the years it has been found impossible to correlate the octane performance of a gasoline in cars on the road using just one type of octane number, and nowadays it is normal to define the anti-knock quality of a fuel by three different octane parameters: research octane number (RON), motor octane number (MON), and a number concerned with the octane distribution

through the boiling range of the gasoline. The most important of these from a commercial viewpoint is the research octane number (RON), since this is widely used to define octane quality in the market. It is determined by the research, or F-1, rating method and relates mainly to relatively mild operating conditions such as are found during cruising and low-speed driving. The motor, or F-2, rating method relates to more severe driving, conditions such as high-speed, high-load operation.

Both motor and research methods are carried out in similar CFR engines using the same standard reference fuels, but with somewhat different test conditions, as shown in Table II.

TABLE II

CFR Knock-Rating Methods—Summary of Test Conditions

	Research ASTM D2699/IP 237	Motor ASTM 2700/IP 236
Engine speed, rev/min	600 ± 6	900 ± 9
Intake air temp., °F	Specified but depends on barometric pressure	100 ± 5
Intake mixture temp., °F	Not specified	300 ± 2
Coolant, °F	212 ± 3	212 ± 3
Compression ratio	Variable	Variable
Ignition advance	13° btdc	14°-26° btdc automatically varied
Knock detection	Detonation meter	Detonation meter
Air intake humidity, grain water/lb dry air	25-50	25-50

The motor method was developed first and was used as the criterion of road performance up to the mid-1930s, since it then gave a good correlation with averaged car ratings carried out at full throttle on a test hill in the USA. In the late 1930s it was found that new cars were rating gasoline nearer to the research method, and since 1949 research octane numbers have been used as the primary parameter for defining octane quality. Nowadays it is accepted that no one octane test can predict road octane performance under all conditions and for all cars.

Most gasolines show a higher research octane number than motor octane number, and the difference between these two octane ratings is called the sensitivity since it affords a measure of the sensitivity of the fuel to changes in operating conditions, i.e.

$$\text{Sensitivity} = \text{RON} - \text{MON}$$

Sensitivity (S) is often used instead of MON and together with RON to define road octane performance.

The third octane parameter used gives a measure of the distribution of octane number through the distillation range of the gasoline. Figure 4 illustrates how two gasolines, having identical research octane numbers, can have quite different octane qualities throughout the boiling range.

The RON of the first half of fuel A which distils off (0-50 per cent) is much higher than that of fuel B and, as heavier and heavier fractions are included, so

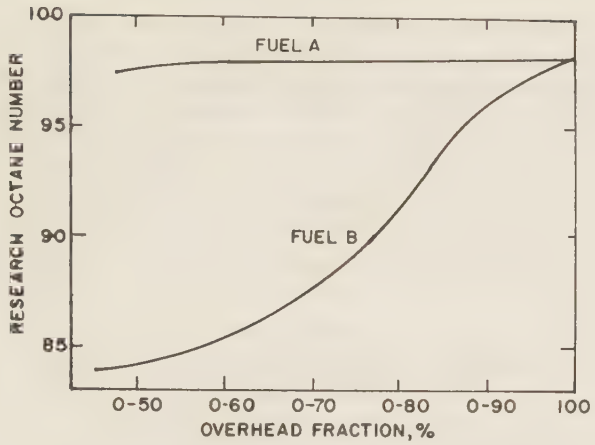

FIG. 4. Possible difference in octane distribution between fuels of same research octane number.

the overall octane levels come together for both fuels. In effect fuel B is composed of a blend of high- and low-octane components, while fuel A tends to be composed of components all of which have similar octane qualities. In practice most gasolines have a lower octane quality in the front or low-boiling end than in the back or high-boiling fraction.

The importance of octane distribution in a fuel is that some cars, particularly during full throttle acceleration, tend to segregate the high-boiling from the low-boiling components in the inlet manifold. This has the effect that, for a brief period, only the lower-boiling components that have been fully vaporized go forward to some cylinders, while the high-boiling materials still in liquid form hang back in the manifold. Since the lighter fraction normally has a lower octane quality than the heavier components, transient knock occurs, which then dies away as the heavier fractions 'catch-up'.

Octane distribution of a fuel can be measured by a number of different methods in the laboratory. One type of test measures the octane number of the lighter fractions that distil off under standard conditions; the most common fraction used is the percentage distilling up to 100°C. The difference between the RON of this fraction and the RON of the total fuel is a measure of octane distribution and is designated as $\Delta R_{100°C}$—often shortened to ΔR. Another method not now used very widely in the oil industry, employs a CFR engine fitted with a special manifold which allows some of the heavier fractions to be segregated before they reach the engine.

Anti-knock additives

In order to achieve the required octane levels in commercial gasolines in the most economical way, anti-knock additives are used. By far the most common of these are the lead alkyls such as tetraethyl lead (TEL) and tetramethyl lead (TML) since, although they were discovered in the early 1920s, no more cost-effective additive for enhancing octane quality has yet been found. The amount added to gasoline in the UK is currently (1983) not allowed to exceed 0.40 g/l of

lead and this limit is to be reduced to 0.15 g/l in January 1986. It is necessary to use scavengers together with lead alkyls in order to ensure that the lead oxides and other compounds formed during combustion do not collect in the combustion chamber as deposits but are removed with the exhaust gases. Without a scavenger, hard deposits can be formed which can flake off and cause valve burning by holding a valve off its seat. Most commonly mixtures of ethylene dibromide and ethylene dichloride are used for this purpose in motor gasoline, and they function by forming volatile lead halides which are readily removed via the exhaust. The composition and characteristics of these lead fluids as used in the UK are as shown in Table III.

TABLE III
Composition and Properties of Lead Fluids

	TEL	TML
Composition, % wt		
Lead alkyl	61.5	50.8
Ethylene dibromide	17.9	17.9
Ethylene dichloride	18.8	18.8
Dye, diluent, inhibitor, etc.	1.8	12.5
Properties		
Boiling point	200°C	110°C
Specific gravity 20/4°C	1.597	1.578

It will be seen that TML has a much lower boiling point than TEL and in fact distils mainly with the lighter 50 per cent of the gasoline. For this reason TML is particularly useful for improving the octane distribution of the gasoline. In many cases TML tends to improve the motor octane slightly more than the research octane level, so that it also improves to a small extent the sensitivity of the gasoline.

There are, in fact, a whole range of lead alkyl additives available, each containing different proportions of the following lead alkyls:

$Pb(C_2H_5)_4$	tetraethyl lead (TEL)
$Pb(CH_3)_4$	tetramethyl lead (TML)
$Pb(C_2H_5)_3CH_3$	triethylmethyl lead
$Pb(C_2H_5)_2(CH_3)_2$	diethyldimethyl lead
$Pb(C_2H_5)(CH_3)_3$	ethyltrimethyl lead

In most cases, however, blends of TML and TEL are used to give the right octane balance to the blend. The optimum lead alkyl to use depends upon the hydrocarbon composition of the blend, and there are cases where it is advantageous to use lead compounds containing alkyls other than TEL and TML.

Generally speaking, low octane number fuels show the greatest response to lead, and paraffinic and naphthenic components have a higher response than olefinic or aromatic stocks. The lead response in terms of research octane number of some typical refinery blend components is shown in Fig. 5. Table IV summarizes the octane levels of a range of hydrocarbons, and also gives some blending numbers which, to some extent, show the effective octane value of the hydrocarbon in a gasoline blend.

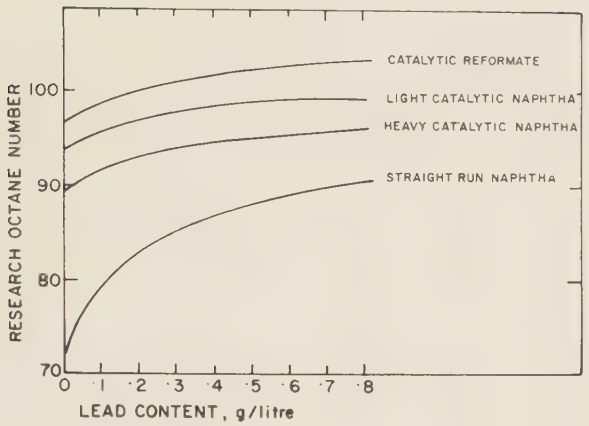

Fig. 5. Lead response of refinery blend components.

The mechanism by which the lead compounds function is quite complex. The active material which reduces knock is the lead oxide that is readily formed as a fine mist and which inhibits pre-flame reactions and therefore auto-ignition. Lead alkyls are effective not just because they represent a convenient form in which to add lead to gasoline, but also because they decompose and oxidize to lead oxide under the combustion conditions occurring in the cylinder. Some other organic lead compounds which do not oxidize so easily have very much poorer anti-knock properties.

Materials are known that change the lead response of lead alkyls. Lead antagonism occurs when sulphur is present in gasoline, because the sulphur reacts with the lead forming lead sulphate, so that under these circumstances the improvement in octane number achieved is not as great as would be obtained with sulphur-free components. Sulphur components vary in the extent to which they adversely influence the effectiveness of lead alkyls, and of those that are found in petroleum, the order of decreasing antagonistic effect is: thiols, disulphides, sulphides, and thiophenes. Lead appreciators are also known which enhance the lead response in fuel, one example of which is tertiary butyl acetate.

Pressures to reduce atmospheric pollution are tending towards the reduction or elimination of lead from gasoline, particularly in North America, Japan, and Europe. There are two main reasons for this. The first is that lead is claimed by some to affect children, even at very low levels. Despite extensive work in this area unequivocal conclusions cannot be drawn. The second reason for eliminating lead is that it acts as a catalyst poison. If it were necessary to use catalytic reactors sensitive to lead to reduce carbon monoxide and hydrocarbon emissions (unlikely in the UK in the near future), the elimination of lead might then become essential. As has been stated, lead is used as the most economical way to achieve high octane levels in commercial gasolines, so that eliminating or reducing lead from an octane viewpoint affects only the cost of gasoline production. The economics operate in two ways. If vehicles are produced requiring a high-octane quality, then the cost of producing such gasolines with low or zero lead will be high due to the additional or more severe

TABLE IV

CFR Octane Numbers of Some Hydrocarbons

Hydrocarbon	Boiling point C	Octane number			
		Actual		Blending	
		Research	Motor	Research	Motor*
Paraffins					
n-Butane	0.5	—	—	113	114
2-Methylpropane	11.7	—	—	122	121
n-Pentane	36.0	62	62	62	67
2-Methylbutane	27.9	92	90	99	104
2.2-Dimethylpropane (neopentane)	9.5	85	80	100	90
n-Hexane	68.7	25	26	19	22
2-Methylpentane	60.3	73	73	83	79
2,2-Dimethylbutane (neohexane)	49.7	92	93	89	97
n-Heptane	98.4	0	0	0	0
2-Methylhexane	90.1	42	46	41	42
2,2-Dimethylpentane	79.3	93	96	89	93
2.2.3-Trimethylbutane (triptane)	80.9	>100	>100	113	113
n-Octane	125.6	—	—	−19	−15
2-Methylheptane	118.1	22	13	24	24
2,2-Dimethylhexane	106.5	72	77	67	76
2,2,3-Trimethylpentane	109.8	100	100	105	112
2,2,4-Trimethylpentane (iso-octane)	99.2	100	100	100	100
Olefins					
Pentene-2	36.4	—	—	152	135
2-Methyl-2-butene (trimethylethylene)	38.5	97	85	176	141
Hexene-1	63.7	76	63	97	94
Hexene-2	68.0	93	81	134	129
3-Methylpentene-2	69.5	97	81	130	118
4-Methylpentene-2	58.8	99	84	130	128
Octene-1	121.6	29	35	—	—
Octene-2	125.2	56	56	75	68
Octene-3	123.2	72	68	95	85
2,4,4-Trimethylpentane-1	101.5	>100	86	164	153
2,4,4-Trimethylpentane-2	104.5	>100	86	148	139
Aromatics					
Benzene	80.1	>100	>100	99	91
Toluene	110.6	>100	>100	124	112
o-Xylene	144.5	>100	>100	120	103
m-Xylene	139.2	>100	>100	145	124
p-Xylene	138.5	>100	>100	146	127
Ethylbenzene	136.5	>100	98	124	107
1,3,5-Trimethylbenzene (mesitylene)	164.6	>100	>100	171	137
Propylbenzene	159.2	>100	98	127	129
Isopropylbenzene (cumene)	152.3	>100	99	132	124

TABLE IV—*contd.*

Hydrocarbon	Boiling point C	Octane number			
		Actual		Blending	
		Research	Motor	Research	Motor*
Naphthenes					
Cyclopentane	49.2		85	141	141
Methylcyclopentane	71.8	91	80	107	99
Ethylcyclopentane	103.0	67	61	75	67
Propylcyclopentane	130.8	31	28	27	27
Isopropylcyclopentane	126.4	81	76	83	81
Cyclohexane	80.8	83	77	110	97
Methylcyclohexane	100.9	75	71	104	84
Ethylcyclohexane	130.4	46	41	43	39
o-Dimethylcyclohexane	123–130	81	79	85	83
m-Dimethylcyclohexane	121–125	67	64	67	65
p-Dimethylcyclohexane	119–125	68	65	66	63
Propylcyclohexane	155.0	18	14	—	—

* 20% vol hydrocarbon in 80% vol 60/40 iso-octane/*n*-heptane.

processing necessary—although the cars themselves will have a relatively good fuel consumption. Conversely, if low-octane lead-free or low-lead gasoline is acceptable by vehicles, although the refining costs will be low, the fuel economy of the cars themselves will be relatively poor.

There are some alternatives to lead alkyls which can be, and have been, used as anti-knock agents. One commercially available material is methylcyclopentadienyl manganese tricarbonyl (MMT), and in spite of its being more expensive than lead alkyl it has been used to improve the octane quality of unleaded gasoline in the USA, although its use is subject to Federal restrictions. There are some problems with this compound in that it is reported to give an increase in the level of unburnt hydrocarbons in exhaust gases and to plug catalysts used for improving exhaust quality, so its large-scale use is unlikely.

Many other organometallic and volatile inorganic materials have been shown to have anti-knock properties (e.g. dicyclopentadienyl iron, nickel carbonyl, etc.), but these have their own problems such as difficulty in scavenging the deposits after combustion, increased cylinder bore wear, etc. and none are likely to take the place of lead alkyls.

Ashless anti-knocks are also known but have to be used at very much higher concentrations than the metallic additives. One which has been used commercially in the past is monomethylaniline, and it has been shown that this material acts as an anti-knock agent in its undecomposed form, but that if it is decomposed too early in the combustion cycle it can even have a pro-knock effect. A difficulty with this amine type of anti-knock additive is its toxicity, and it is unlikely that it could be used nowadays for this reason.

Octane blending

Octane numbers do not blend linearly, so that it has been necessary for refiners to develop quite complex blending calculation methods involving the use of Octane Blending Numbers, in order that linear blending can be achieved. The

presence of lead alkyls complicates the blend calculations, since different blend components have different lead response curves, i.e. a given amount of lead shows quite different increases in octane level in different components as was shown in Fig. 5. There can also be synergistic or antagonistic effects between blend components, which are often taken into account by applying factors to Octane Blending Numbers or by using other correction terms.

Normally each refinery develops its own blending data based on its experience with the blend components it has available, and the data developed by one refinery would not necessarily be of any great value to another.

5.6 Anti-knock Requirements of Cars

So far we have discussed the laboratory measurement and definitions of anti-knock quality of fuels. We now have to consider the application of these to cars on the road. First of all, the major design, operating, and other conditions that influence knock will be summarized. These are:

(i) Compression ratio

Increasing compression ratio increases the octane needs of an engine, and a correlation which has been obtained from practical data[6] is shown in Fig. 6.

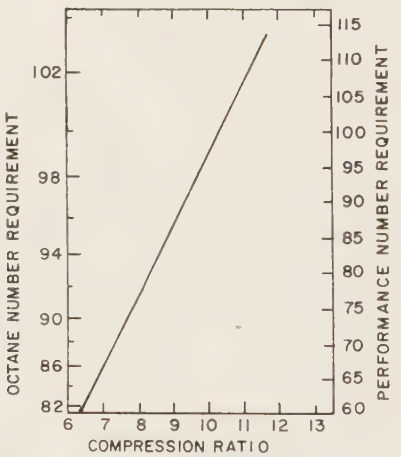

Fig. 6. Influence of compression ratio on octane requirements.

In this plot octane requirement is shown both in terms of octane number, which is a non-linear scale, and in terms of performance number, which is linear. Performance number is an empirical relationship derived to give a linear correlation with compression ratio that permits extrapolation beyond the range for which practical data are readily available. The correlation between compression ratio and octane requirement is an extremely approximate one when considering results obtained on a range of cars of varying compression ratio. This is because of the multiplicity of other factors influencing octane requirement, and because of manufacturing tolerances. The latter feature is

important in causing apparently identical cars to differ quite widely in their octane requirements.

(ii) Ignition timing

The tendency to knock increases as spark advance is increased, an example of which, for a specific car, is shown in Fig. 7.

Although it is possible to make large changes in octane requirements by adjustment of the spark advance mechanism of a car, it must be remembered that maximum power is influenced significantly if the spark timing is moved too far from the optimum.

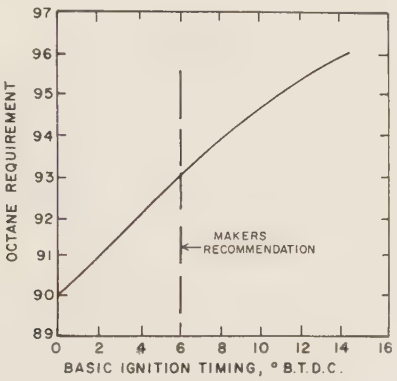

FIG. 7. Influence of ignition timing on octane requirement.

Each car model differs quite widely in its ignition characteristics. Figure 8 shows an ignition distributor spark advance curve for a particular car, and shows for two fuels, A and B, the minimum spark advance that just gives trace knock as engine speed is increased.

It will be seen that fuel A is quite close to a knock situation at low speed, but is a long way off at high speed. However, it is also possible to get the situation shown by fuel B. This fuel is very satisfactory at low engine speeds, but as the speed increases it performs less well relative to the spark advance and in fact knock occurs over the range 3300 to 5100 rev/min. Such a fuel would have a poor motor octane number in relation to its research octane number, i.e. would have a high sensitivity.

Fuel A is a satisfactory fuel for this particular car. If a fuel of similar sensitivity to fuel A but at a lower research octane level were used, then the curve for this fuel would be displaced downwards and knock would occur at low speeds but not at high speeds. This same effect could be obtained by using a fuel with a poor octane distribution (i.e. a high ΔR level). When tested under accelerating conditions such a fuel gives a poor octane performance at low speeds, but can be quite satisfactory at higher speeds. This is a common penalty of using too low an octane quality in a car. If a fuel of the same sensitivity as fuel B were used, but at a higher research octane level, then such a fuel would be out of knock at all speeds and would be entirely satisfactory. Research octane number is only one factor in influencing whether a car is out of knock or not,

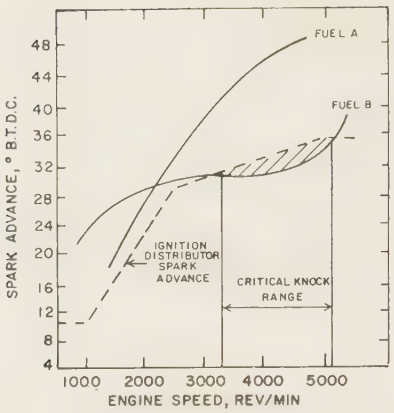

FIG. 8. Knock-limited spark-advance curves for different fuels.

and the other factors of motor octane number and octane distribution ($\Delta R_{100\ C}$) must also be considered. The overall anti-knock quality of a gasoline is a combination of its research octane level, its motor octane number, and its octane distribution.

Knock at low speed is normally not considered to be serious from the point of view of performance or of possible damage to the engine, and since it is fairly readily apparent to the experienced driver, it is a useful indication that too low a grade of fuel is being used. High speed knock on the other hand cannot easily be heard because of wind, engine, and road noises, and could occur for long periods of time in motorway driving. Under these conditions it is possible for engine damage to occur. Such damage usually takes the form of piston erosion, top piston land failure, or head gasket failure.

(*iii*) *Speed*

Normally an increase in engine speed reduces the knocking tendency, because less time is available for pre-flame reactions to take place, and also because increased turbulence in the charge accelerates complete combustion. However, in modern cars the timing of the spark advances as engine speed increases in order to ensure that maximum power is obtained at all speed ranges, so that high-speed operation can sometimes be as critical as low-speed operation.

(*iv*) *Temperature*

Increase in engine temperature, and particularly charge temperature, increases the tendency to knock, as would be expected from a consideration of the mechanism of knock as an end-gas explosion. The motor octane method has a much higher charge temperature than the research octane method, and consequently most fuels have lower MON than RON levels. Fuels of low sensitivity, by definition, are influenced to a much smaller degree than fuels of high sensitivity by such temperature changes.

(v) Load

Because increasing load raises the engine temperature and end-gas pressure, the likelihood of knock correspondingly becomes greater with increasing load.

(vi) Mixture strength

The tendency to knock varies with mixture strength and is greatest around 13.5:1 air/fuel ratio. However, the mixture strength for maximum knock varies somewhat from one fuel to another.

Measurement of octane requirements of vehicles

The octane requirement of a car is usually defined as the octane number of a fuel that just gives trace knock in that car. However, because knock is dependent on operating conditions it is necessary to state the test conditions under which the octane requirement measurement is carried out. In addition, because cars vary in the extent to which they respond to different fuel octane parameters, it is also necessary to define fully the fuels used.

Usually it is the maximum octane requirement that is of most interest, i.e. the highest research octane number of a specified fuel type (fuels can be divided into types, e.g. having low sensitivity, high $\Delta R_{100°C}$, etc.) that gives trace knock when the car is subjected to a range of different test conditions. Octane requirements can be determined in terms of primary reference fuels (i.e. blends of iso-octane and *n*-heptane) or in terms of full boiling range fuels (i.e. commercial type gasolines that at a constant research octane number can vary widely in their motor octane number and octane distribution).

It is not obvious which type of operating condition will give the maximum octane requirement in a car. It is very often found under full-throttle accelerating conditions from low starting speeds using the highest gear available, but it can occur also under part-throttle accelerating conditions or even under constant speed conditions.

Standard test procedures have been developed by the Cooperative Octane Requirement Committee for use both on roads and on dynamometers.[7]

A development over the past few years has been to fit knock sensors to some engines, particularly if they are turbocharged, in order to protect the engine from knock damage. When knock is detected, the octane requirement of the vehicle is automatically reduced for a set period of time, often by retarding the ignition, although other methods can be used. The octane requirement of such vehicles is then the octane level at which no further retardation, etc. is possible. When such a vehicle is retarded as a result of using a low-octane quality fuel, it may have a reduced power output compared with the non-knocking situation. This in turn, can result in an increase in fuel consumption.

Octane rating of fuels using vehicles

Fuels are rated in the CFR engine by comparing their performance with primary reference fuels. Fuels can also be rated in cars on the road in a somewhat similar way. The octane numbers thus obtained are often called

road octane numbers. Fuel ratings differ from octane requirements in that requirements are measured at a fixed ignition timing (so that a series of fuels is needed increasing in steps of one octane number), whereas in fuel ratings the ignition is varied to give trace knock with the fuel under test.

There are two standard test procedures in common use for rating fuels in cars. The first is the Modified Uniontown Procedure. Here instrumentation is required for adjusting and measuring basic ignition timing. Full-throttle accelerations are made from a low speed using primary reference fuels, the basic ignition timing being adjusted so that a level of knock not greater than trace is obtained during any part of the acceleration. A curve is thus developed for spark advance versus octane number of the reference fuel (designated road octane number) at the trace knock level as shown in Fig. 9. The test fuel is then run in the same way, and the road octane number corresponding to the trace knock ignition setting is read off this curve. This procedure is rapid and simple to carry out, but does not give very much information about how the octane rating changes over the speed range of the car.

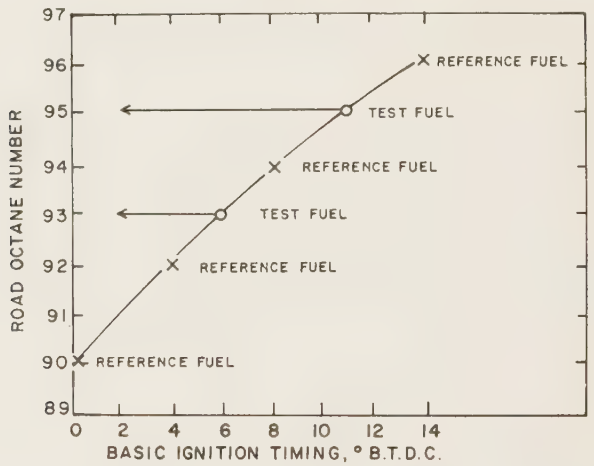

Fig. 9. Modified Uniontown curve.

The Modified Borderline Knock Procedure is the second commonly used rating procedure and this does allow octane ratings to be investigated over the speed range of the car. The automatic spark advance mechanism of the car is put out of action and arrangements are made to adjust it manually during acceleration. Accelerations are made as in the Modified Uniontown Procedure but the spark timing is continually adjusted manually in order to maintain knock intensity at the trace level throughout the acceleration. The data obtained can be handled in a number of ways. One method is to construct a framework of ignition timing against engine speed for a series of primary reference fuels, so that the road octane numbers of the test fuels can be read off at any speed level, as shown in Fig. 10. Here it will be seen that fuel 1 has a higher road octane number than fuel 2 at low speeds and a lower value at high speeds.

Both of these methods are 'modified' from earlier procedures. The borderline procedure (i.e. not modified) is probably no longer used, and involves retarding the ignition timing and noting the speed at which knock dies out in a full-throttle acceleration. This whole procedure is repeated at increasing spark advance settings until again a framework of trace knock against ignition timing for the test fuel and primary reference fuels is built up.

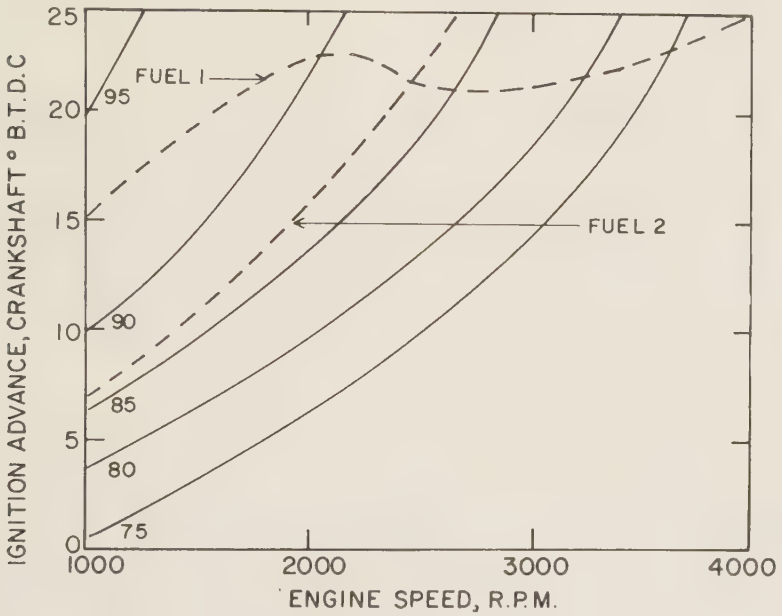

Fig. 10. Determination of road octane number by Modified Borderline Knock Procedure.

Influence of combustion chamber deposits on knock

During operation deposits tend to accumulate in the combustion chamber. They are partly organic and partly inorganic, and are derived from both the fuel and the lubricant. The volume of deposits in a combustion chamber does not increase indefinitely, but reaches an equilibrium condition because of flaking due to high temperature gradients and thermal stresses within the deposit thickness. It normally requires about 3000 miles for deposits to reach an equilibrium condition, and even then substantial changes in the mode of driving can have a marked effect on the amount. City type driving, i.e. low-speed, stop-start operation, favours deposit formation, while extended high-speed driving tends to burn away deposits.

As might be expected, combustion chamber deposits significantly influence octane requirement and give rise to the phenomenon known as Octane Requirement Increase (ORI). The increase in octane requirement from a clean engine to the equilibrium deposit condition is commonly anything from 1 to 8 octane numbers (RON or MON), and can be even higher. The reasons for

this ORI effect are:

(i) The deposits reduce the combustion chamber volume, thereby increasing compression ratio.
(ii) The deposits reduce thermal conductivity, thereby increasing combustion chamber temperatures.
(iii) The chemical nature of the deposits may catalyse those reactions known to favour detonation.

Influence of atmospheric conditions on knock

The atmospheric conditions which influence knock are temperature, humidity, and pressure. Quite wide variations can occur between different cars, although the directional effects are always the same. In a study on a limited number of US cars[8] it was found that an increase in temperature raised octane requirement on average by 0.044 ON/°F, and an increase in absolute humidity lowered octane requirements by an average of 0.045 ON/gr/lb. A later investigation gave similar values, i.e. 0.054 MON/°F and −0.035 MON/gr/lb increase in humidity. The effect of increasing altitude was found to be non-linear, but on average the octane requirement decreased by 4.1 numbers from sea level to 3000 ft and by 7.5 numbers from 3000 to 6000 ft.

Methods of using octane data

When octane requirements are determined on a number of apparently identical cars, each of which has had its ignition set to maker's recommendation, it is almost invariably found that the requirements show spreads of anything between about 5 and 15 octane numbers (RON or MON). It is impossible then to know accurately the octane requirement of any particular car without actually testing it, and one can only draw a curve showing the distribution of determined octane requirements for a model, as shown in Fig. 11.

The reasons for this arise from production tolerances giving rise to different compression ratios and ignition system characteristics, variations in carburation, differences in the amount of combustion chamber deposits, changes in atmospheric conditions during testing, etc.

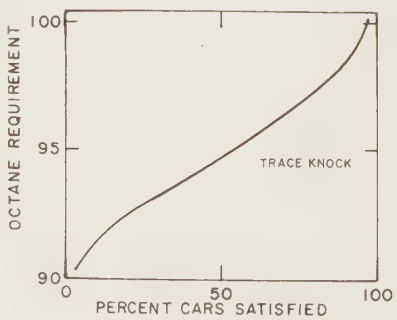

Fig. 11. Distribution of octane requirements for a single car model.

The octane distribution curves that can be drawn vary enormously from model to model. In some cars the range of requirements is small so that the distribution curve is relatively flat; in others the range may be large. The average requirement level depends on such factors as nominal compression ratio, ignition timing, etc. Automatic transmission versions of cars tend to have lower average octane requirements than the corresponding manual versions, since the vehicle cannot normally be subjected to hard accelerations from low engine speeds in top gear.

Because of this marked lack of uniformity, even between cars of the same model, it is necessary for oil companies to test large numbers of cars in order to assess the octane needs of a market, and this testing is normally carried out cooperatively and the results pooled. One method of handling such data is to present them in the form of 'satisfaction curves', both for car models and for whole car populations, so that the gasoline marketer is in a position to know the percentage of cars satisfied by each grade of gasoline he markets.

Octane requirement data and fuel rating data can also be used to determine the way in which a car responds to the different octane parameters. Equations for car models or car populations can be derived of the form

$$\text{Road ON} = a(\text{RON}) + b(\text{MON}) + c\Delta R + d$$

where a, b, c, and d are constants.

The equation form quoted above would refer to a given test procedure, and the coefficients could be quite different under different test conditions. The coefficient for MON is often relatively small compared with the coefficient for RON under cruising or low speed acceleration conditions, and the MON coefficient usually increases with increasing speed and load. Similarly, the coefficient for ΔR is only of significance in accelerating conditions.

For cars, instead of using road octane numbers, equations can also be derived in terms of ignition timing to give trace knock, i.e. knock-limited spark advance (KLSA).

Equations can also be developed using terms other than those quoted above. Olefin content instead of, or as well as, sensitivity has been used. Aromatics, lead, and sulphur contents are other terms which have been included in these road octane equations.

5.7 Abnormal Combustion

There are a number of other abnormal combustion phenomena that occur in spark-ignition engines, apart from knock.

Preignition

Preignition occurs when the charge is ignited prematurely, and this can be caused by glowing deposits or by a hot exhaust valve or spark plug. Deposit-induced preignition (DIPI) is of a somewhat random nature. Having begun, it may die out as deposits burn off or it may increase in severity and produce mechanical damage; the latter is called Run-away Surface Ignition (RSI). RSI is a violently unstable condition in which ignition occurs so early that the heat of combustion cannot be converted into useful mechanical work. The excess heat can burn a hole in a piston in a very short time.

It is mainly engine design that determines whether or not an engine is prone to preignition, i.e. such factors as exhaust valve design and cooling, spark plug position and heat range, etc. Engine operating conditions such as ignition timing, mixture strength, speed, load, and mode of operation largely determine the severity of preignition in an already critical engine.

Engines differ in their susceptibility to preignition, and their relative resistance to this problem can be evaluated by running them first under a fairly light load cyclic condition to lay down deposits and then under sustained high-speed/high-load operation. The onset of preignition can be detected in a variety of ways, e.g. fall in power output, increase in peak pressure, increase in temperature, presence of a flame front before ignition by the plug (as indicated by an ionization gap), displacement of peak pressure curves, etc.

Fuel variables in normal commercial gasolines are relatively minor factors in influencing the severity of preignition in a critical engine. Deposit-induced preignition is of most importance when considering the effect of fuel variables, and here two properties of the fuel are involved, the tendency of the fuel to be ignited by glowing deposits, and the deposit-forming tendency of the fuel.

Different fuels have been rated for their preignition tendency by the Ricardo method[9] in which a hot spot or preigniter, consisting of an electrically heated coil of wire, protrudes into the combustion chamber roughly opposite to the spark plug. The amount of electrical energy to cause preignition is used to define the pre-ignition tendency of the fuel. A rating scale is used in which iso-octane (having a high resistance to preignition) is given an arbitrary value of 100 and cyclohexane (low resistance to preignition) is given a value of zero. Extrapolation is used to fix ratings outside the scale 0–100.

This method of rating fuels for their preignition tendency only measures the tendency for hot surfaces or glowing deposits to ignite the fuel. It does not measure the deposit-forming tendency of the fuel.

As indicated above, the susceptibility of fuels to preignition is influenced both by the deposit-forming tendency and by the ignition tendency of their constituent hydrocarbons. From a deposit-forming viewpoint, heavy, high-boiling point hydrocarbons such as heavy aromatics are bad and tend to increase preignition. Regarding ignition tendency, pure hydrocarbons, even of the same chemical type, vary enormously, e.g.

Aromatics	Benzene (26 on Ricardo scale) is poor, but toluene (93) and xylenes (>100) are good.
Naphthenes	Cyclopentane is good (70), while cyclohexane (0) is poor.
Olefins	Di-isobutylene is good (64), but hexene-2 (-26) is very poor.
Paraffins	All are good and mainly in the range 50–100.

Most refinery gasoline blend components fall within the range 40 to 90 (without lead). Finished gasolines all normally lie quite close together in their ratings.

TEL and TML have a dual influence in that they improve the resistance of fuels to preignition by glowing deposits, but increase combustion chamber deposits so that the deposit-forming tendency often outweighs the auto-ignition benefit.

Phosphorus in the form of an organic ester was commonly added to gasoline at one time, mainly as an anti-misfire additive but also to reduce preignition.

This additive increases the thermal conductivity and melting point of deposits, and reduces preignition by deposits by reducing their glowing tendency. Unfortunately this additive also had a tendency to reduce octane quality. Boron additives are also claimed to reduce preignition, as are the little used manganese anti-knock additives and the lead appreciator, tertiary butyl acetate.

There is no direct correlation of anti-knock quality with preignition. It is a fact, however, that high temperatures favour both preignition and knock, and that one may lead to the other. Thus under high-speed conditions if an engine is knocking the resultant increase in temperature can lead to preignition; conversely if the engine is preigniting, then knock sometimes follows, again because of the increase in temperature.

Misfire

Apart from mechanical failure of the ignition system, the most common cause of misfire is fouling of the spark plug by deposits. Two types of failure can be experienced:

(i) Gap bridging, where a deposit forms across the spark gap, thus preventing the firing of the plug under all operating conditions.

(ii) Plug shorting caused by deposits of lead salts on the ceramic having high electrical conductivity under high-temperature conditions, thus allowing the current to leak away. This effect can be overcome to some extent by the use of phosphorus additives in the fuel which retain their electrical resistance at temperatures well above those found in practice. The compounds identified in spark plug deposits and their normal position on the ceramic insulation for an engine operating with fuel containing phosphorus are shown in Fig. 12.

Other additives are known which are claimed to reduce combustion chamber and spark plug deposits, thereby reducing the extent of misfire.

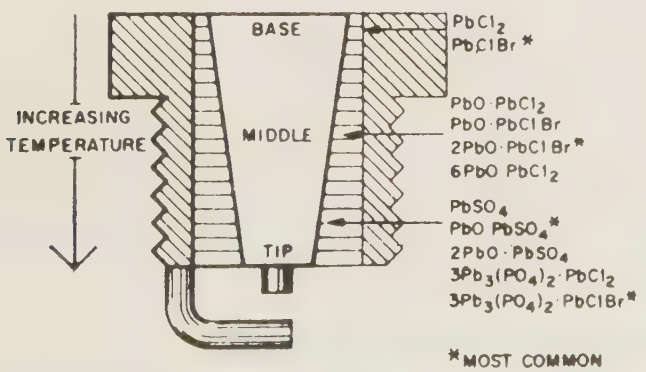

FIG. 12. Composition and location of lead compounds deposited on a sparking plug with a fuel containing a phosphorus additive.

Run-on

This is the tendency for an engine to continue firing after the ignition has been switched off. It is most often the result of spontaneous ignition of the fuel/air charge, and is much less frequently caused by surface ignition from hot spots in the cylinder.

When a fuel/air mixture is compressed, if the temperature is high enough, pre-flame reactions take place which can result in spontaneous ignition. In an engine there is a limited range of speed, cylinder pressure, and temperature over which this spontaneous ignition is likely to occur. If the speed is too high there is insufficient time for the pre-flame reactions to take place, and if the temperature is too low the pre-flame reactions will not take place rapidly enough. Thus when an engine is switched off, if the speed and temperature come within the critical region for spontaneous ignition, the engine will refire. This may result in the temperature and speed increasing out of the critical region, so that the engine may not fire again for one or two cycles, that is, until conditions are again within the critical region. Run-on is characterized by this rather erratic running of the engine, and its duration is limited by the overall cooling of the whole engine.

The major mechanical factors that adversely influence run-on are inadequate cooling of the combustion chamber at low speeds, and the use of too high an idle speed since this gives a higher cylinder pressure resulting from the increased throttle opening. As a last resort cure, fuel cut-off valves can be fitted. The fuel factor which is of prime importance in overcoming run-on is its resistance to spontaneous ignition, so that the fuel should have an adequate octane level. It is by no means rare for an engine to require a higher RON to overcome run-on than to overcome knock.

Other abnormal combustion phenomena

Other abnormal combustion phenomena have been observed and documented having such titles as wild ping and rumble. They are all variations of early ignition by deposits or other hot surfaces, and detailed descriptions of these will be found in the literature dealing with abnormal combustion.[10]

6 GASOLINE VOLATILITY

The volatility of gasoline has a vital influence on the performance of a vehicle. It affects the ease of starting, the time taken to warm-up, the tendency to stall and suffer power loss due to ice formation in the carburettor; it influences also the vapour-locking tendency, and is an important factor in determining overall fuel economy. The volatility required for any given season and location will need to take into account the normal range of ambient temperature, pressure (i.e. altitude), and humidity experienced. Since cars vary widely in their response to gasoline volatility, the car population at the relevant location must also be taken into consideration.

6.1 Characterization of Gasoline Volatility

Motor gasoline does not have a single boiling temperature since it is a mixture of very many hydrocarbons (often more than 300), each of which has its own

boiling point. The boiling points of these component hydrocarbons lie mostly in the range 30°C to 250°C. One way, therefore, of expressing the volatility of a gasoline is by means of its distillation curve, and a standard test procedure is available for this (ASTM D86 or IP 123). Figure 13 shows some distillation curves for a number of different types of gasoline.

The distillation curve of a gasoline is often roughly divided into three parts. The front-end is that portion distilling up to about 70°C. The mid-fill is the part extending from about 70°C to 150°C. Finally, the back-end is the material boiling above about 150°C.

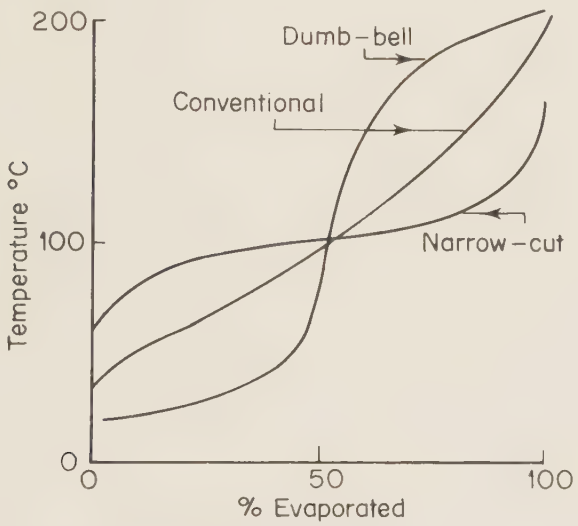

Fig. 13. Gasoline distillation curves.

Most gasolines in the market have distillation curves that are roughly parallel to the conventional volatility curve in Fig. 13. So-called dumb-bell fuels are blends of light and heavy components with very little material boiling in the mid-fill range and so have rather steep distillation curves in this area. Narrow-cut blends have most of their hydrocarbons boiling at about the same temperature, and so have flat distillation curves. Narrow-cut and dumb-bell blends can behave in vehicles quite differently from fuels having conventionally shaped distillation curves.

Usually specific points on the distillation curve are selected to characterize gasolines. These can be the percentage evaporated at set temperatures, such as 70, 100, 150, and 180°C, and are often then designated as E70, E100, E150, and E180. Equally the temperatures at which various percentages are evaporated can also be used, e.g. T50 is the temperature at which 50 per cent is evaporated.

Another widely used measure of volatility is the vapour pressure and a standard test (Reid Vapour Pressure—ASTM D323 or IP 69) is used to define this parameter. It is carried out at a temperature of 37.8°C in a container having a 4:1 ratio of air to liquid. The range of Reid vapour pressures found in practice is from about 7 to 15 lb/in^2 gauge (approximately 0.45 to 1.05 bar).

A further volatility measure, of most interest in defining the front-end volatility, is the Vapour/Liquid Ratio (V/L) at temperatures which relate to those found in the critical parts of a fuel system (ASTM D2533).

6.2 Conflicting Requirements of Gasoline Volatility

Care must be taken to ensure that volatility is controlled to within reasonable limits over the whole distillation range. As already indicated, the limits for any given country or area at any given season are set by considerations of climate, driving conditions, and the susceptibility of car models used in that area to volatility-induced problems. Sometimes the volatility to overcome one problem may conflict with that to overcome quite a different problem, so that setting a volatility specification may well involve finding the best compromise. Thus hot weather and/or high altitudes will call for a relatively low volatility fuel to prevent excessive vaporization in the fuel system of those cars prone to vapour lock. However, if some cars in the area are also prone to cold-starting problems, it is difficult to know how much low-boiling component to include in the fuel. Similarly a low volatility fuel is not prone to carburettor icing, but gives poor warm-up and cold weather driveability. Again, the high-boiling components are valuable in giving good fuel economy because of their high heat content, but they tend to increase combustion chamber deposits and to degrade the lubricating oil.

Figure 14 illustrates these conflicting influences in terms of the gasoline distillation curve.

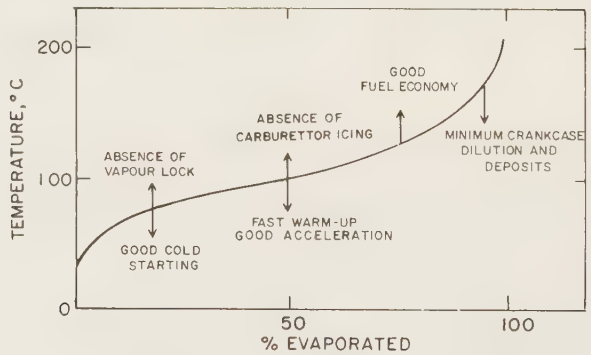

Fig. 14. Influence of gasoline volatility on car performance.

6.3 Cold Starting

An inflammable mixture of fuel vapour and air must be present in the cylinder of an engine in order that it may start. When the engine is cold this is obtained by the use of the choke whereby a rich mixture (up to about 1:1 liquid fuel/air ratio) is supplied by the carburettor. This ensures that sufficient fuel is present in the inlet manifold that, even on cold days, enough vaporizes to give a fuel/air ratio that will ignite.

There are a number of factors relating to both engine design and fuel quality that influence ease of starting. Critical factors of the engine are cranking speed

and degree of fuel atomization in the carburettor. To some extent these are complementary, since a high cranking speed causes air to be drawn through the carburettor at a high velocity, and this favours efficient atomization of the fuel in the carburettor and the inlet manifold. The high cranking speed also results in frequent compressions which generate heat and assist in warming up the engine. Battery condition is also important in cold starting, particularly since the efficiency of a battery drops off with decreasing temperature. At 0 °C a new fully charged battery has only 60 per cent of the power available at 25 °C, and at −17 °C it can supply only about 46 per cent of its rated power. The ignition system is another significant factor in that it is necessary to provide a spark of sufficient energy to ignite the fuel/air mixture. A further aspect which is vital for ease of starting is to have a lubricant of the correct low-temperature viscosity, so that in cold weather high cranking speeds are readily obtainable.

The contribution of the fuel to easy starting is usually a minor one compared with the mechanical and lubrication factors mentioned above. It is necessary to have a volatility sufficiently high to provide enough vapour under the temperature conditions prevailing to give an ignitable mixture. Because of this it is the low-boiling components of gasoline that are most important in cold starting. The commonest terms used to correlate front-end volatility with cold-start performance are per cent evaporated at 70 °C (E70), the temperature at which 10 per cent evaporates (T10), the slope at the 10 or 15 per cent evaporated point, the Reid Vapour Pressure (RVP), or a combination of more than one of the above factors. All of these alternatives are usually highly intercorrelated in commercial gasolines, so that the choice of which to use is not a question of very great differences in the accuracy of prediction of cold-start performance, but more a historical association by an organization with a particular parameter.

Figure 15 shows the determined starting time for a European car as a function of ambient temperature for three gasolines differing in front-end volatility. However, it must be stressed that vehicles can differ widely from model to model in their cold-starting characteristics.

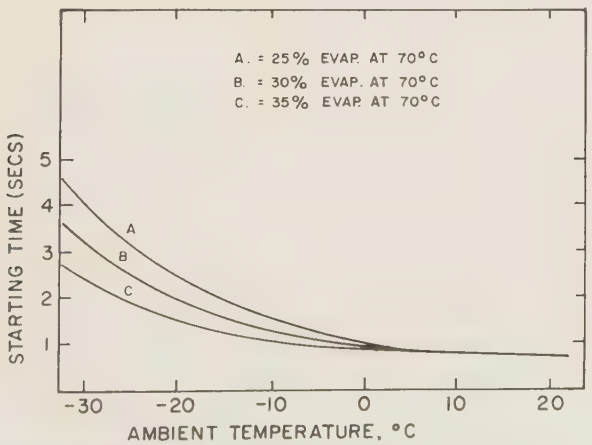

Fig. 15. Influence of ambient temperature and gasoline volatility on cold-starting time.

It will be seen that for this car starting is not dependent to any significant extent on fuel volatility at ambient temperatures above about $-10^{\circ}C$. It is also clear that, purely from a cold-starting viewpoint, gasoline quality improves with increasing front-end volatility. This is in direct opposition to the fuel properties necessary to avoid vapour handling problems. For geographical areas where there is a wide variation between maximum and minimum temperature within a fairly short period it may be difficult to control both vapour lock and cold start.

For vehicles where the design permits the possibility of excessive heat soak-back from the engine to the carburettor, it can happen that with fuels containing a high percentage of low-boiling hydrocarbons, these will be evaporated from the carburettor float chamber leaving behind a comparatively non-volatile fuel for the cold start. Under these conditions an apparently high-volatility fuel can give rise to poor cold-starting performance. It is important therefore to use a test procedure for evaluating cold-start performance that involves allowing the fully warmed-up engine to cool to the test temperature with the gasoline under test already in the fuel system. Changing fuels when the engine is cold can give misleading results.

6.4 Cold Weather Driveability

In cold weather cars can take a very significant time to warm up, i.e. be capable of smooth, non-hesitating accelerations without the use of the choke. It is clearly desirable to achieve this state of affairs quickly, not only to be able to make use of the full power of the engine as soon as possible, but also because excessive use of the choke can have a disastrous influence on fuel consumption, particularly for short journeys, and on exhaust emissions. It also upsets lubrication to some extent, first by increasing the amount by which the lubricant is diluted by gasoline, and secondly by liquid gasoline in the combustion chamber washing lubricant from the upper cylinder walls.

Cars vary widely in the time they take to warm up and also in their sensitivity to the effects of changes in gasoline volatility on warm-up time. This is in spite of the use of inlet manifold 'hot spots', heated by exhaust gases or engine coolant to help vaporization.

Warm-up performance can be measured in a number of different ways. One commonly used procedure developed by the British Technical Council[11] is to measure full throttle acceleration times and smoothness of acceleration during each of a series of consecutive driving cycles (Fig. 16).

The time to achieve stable and consistent acceleration times is a measure of the warm-up performance.

As might be expected, warm-up is strongly influenced by ambient temperature and is improved by increasing gasoline volatility. The fuel parameter that is found to have the greatest influence on warm-up for most gasolines is the mid-boiling range volatility as characterized by, for example, the 50 per cent distillation temperature (T50) or the per cent evaporated at $100^{\circ}C$ (E100). The lighter and heavier components also have some influence on warm-up, but usually to a rather smaller extent.

Even after the car has warmed up, fuel volatility can still have an influence on acceleration time. This is because when the throttle is opened suddenly some

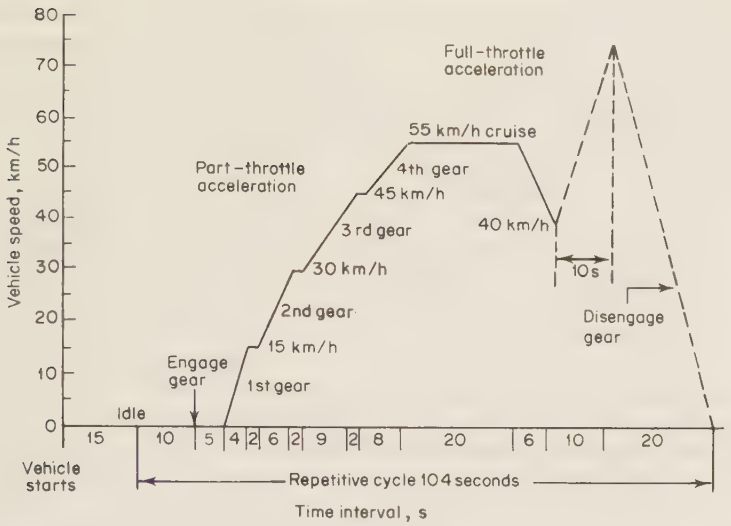

FIG. 16. Cold weather driveability cycle.

of the fuel tends to remain as a liquid on the manifold walls, and the greater absolute pressure under wide open throttle conditions does not help rapid vaporization. In addition, for fixed jet carburettors the flow of air increases more rapidly than the flow of fuel. Thus lean mixtures can be obtained at the beginning of an acceleration. An accelerating pump in some carburettors compensates to some extent for these effects by supplying extra fuel into the air stream as the throttle opens.

In order to obtain maximum power and optimum acceleration performance it is necessary for the extra fuel to vaporize sufficiently in the inlet manifold to give an air/fuel ratio of about 12:1. Low volatility fuels obviously give leaner mixtures, and at mixture strengths above about 15:1 acceleration performance can fall off quite rapidly.

6.5 Hot Weather Driveability—Vapour Lock

When the volatility of a gasoline is too high and/or when high temperature/low pressure conditions prevail, bubbles of gasoline vapour can be formed at critical points in the fuel system. This prevents an adequate supply of fuel to the engine, either by preventing the fuel pump from supplying sufficient fuel to the carburettor bowl or by boiling of the fuel in the carburettor bowl itself. The latter effect is known as percolation and gives rise to a build-up of pressure in the float chamber which the vent hole is unable to cope with, so that liquid gasoline is forced into the inlet manifold, resulting in a surplus of fuel in the manifold and a shortage of fuel in the carburettor. These conditions can make restarting difficult. Percolation is most common after a high-speed run followed by a short stop during which there is excessive heat soak-back to the carburettor from the engine. The whole phenomenon of the fuel system being unable to handle vapour formation is known as vapour lock.

Vapour lock has a number of unwelcome effects on engine operation apart

from difficulties in restarting a hot engine. It can cause uneven running and stalling when a hot engine is at idle; it can cause loss of acceleration performance and can give rise to reduced power at high speeds. The latter effects result from the engine running lean because it is being starved of fuel.

The factors which influence vapour lock are:.

1. The general susceptibility of the car to give rise to vapour in the fuel system and the ability of the fuel system to handle this vapour. This is clearly a function of car design. Important design features which influence the susceptibility of a car to vapour lock are the characteristics of the fuel pump, whether fuel lines liable to be heated by the engine are on the discharge or intake side of the pump, the extent to which heat soak-back affects critical parts of the system, and the general resistance to flow of the whole fuel system.
2. Operating conditions are also important such as the type of driving, e.g. a high-speed run followed by a period at idle or with the engine stopped is a critical operation from a vapour lock viewpoint. Weather conditions also come into this category. High ambient temperatures give rise to higher fuel system temperatures than normal, while low atmospheric pressure, which can be encountered on mountain roads, will lower the temperature at which gasoline will vaporize.
3. The volatility characteristics of the fuel. The degree to which a fuel is liable to give vapour lock depends mainly on its front-end volatility. A number of different front-end volatility parameters have been used to define the vapour locking tendency of a fuel, such as RVP, percentage evaporated at 70°C, the 10 or 15 per cent slope of the distillation curve, the vapour/liquid ratio at a given temperature and pressure, etc. Quite often a combination of some of the above parameters is used, as for example:

$$\text{VLI} = \text{RVP} + 0.10\ (\text{percentage evaporated at } 70^\circ\text{C})$$

where VLI is a vapour lock index, i.e. a measure of the susceptibility of a fuel to give vapour lock.

It has been shown[12] that many of the indices used to control front-end volatility, such as the one given above, are related to the temperatures at which certain vapour/liquid ratios occur, and that although a number of different indices exist they are all equally valid for predicting the susceptibility of a fuel to cause vapour-lock problems.

There are a number of methods of testing cars to determine their vapour-locking tendencies,[13] but generally all of them involve a warm-up period to raise the temperature of the engine and fuel system of the car, followed by a soak period with the engine either at idle or switched off. A timed acceleration is then carried out and a significant increase in acceleration time or in malfunctions during acceleration, idle or in re-starting the engine as compared with the performance using a low-volatility reference fuel, is a measure of vapour lock. These tests can be carried out under closely controlled conditions in which the car is run on a chassis dynamometer (to simulate the road) in a temperature-controlled room so that the ambient temperature at which vapour lock starts to occur can be accurately measured. Tests can also be carried out on

the road and in some cases the heat-soak period takes place in a closed garage or with screens round the engine to minimize the effect of any wind and to improve the repeatability of the test.

In summary, the factors which a gasoline supplier must take into account in order to minimize vapour-lock problems are the susceptibility to these problems of the car population under consideration, the ambient temperature conditions prevailing, and the altitude and severity of the road system in the area considered.

It is usually necessary to market gasolines with different front-end volatilities in summer than in winter and different volatilities may also be necessary in different parts of a country.

6.6 Evaporation Losses

The front-end volatility of gasoline is important for a number of car performance criteria as we have seen. It is also important because it controls evaporation losses which influence such aspects as gasoline quality reaching the customer, economy of manufacture, and air pollution.

Losses of light ends in gasoline storage and distribution can be significant, although a great deal of effort has been made by manufacturers in the design of tanks, etc. to ensure that such losses are minimized. Leakage of hydrocarbon vapour into the atmosphere is undesirable, not only because it represents an economic loss, but also because it increases fire hazard and contributes to atmospheric pollution. Small losses are, however, inevitable when dealing with such a volatile material as gasoline, and it is necessary to take predicted losses into account when manufacturing a gasoline, so as to ensure that the customer receives a product of the correct volatility.

Evaporation losses from the car itself are not usually serious, and represent only a minute fraction of the overall vehicle emissions. Any reduction in gasoline volatility to minimize such losses could influence adversely cold start and warm-up of cars critical to these performance aspects. Evaporative loss control devices are being fitted to cars for use in some countries. One type operates on the principle that hydrocarbon vapours which would normally be lost to the atmosphere are adsorbed in an activated charcoal bed and are later desorbed by an air purge stream back into the engine during acceleration or high-speed cruise operation.

Evaporation losses can, of course, have a small influence on fuel economy. If a car is used for short runs, evaporation from the carburettor with some models can be significant during the periods between runs, particularly at high ambient temperatures and if there is a lot of air movement around the carburettor and tank.

The fuel parameter which has the greatest influence on evaporation losses is the vapour pressure, although the front end of the distillation curve is also quite often taken into account when predicting such losses.

6.7 Carburettor Icing

Ice formation in carburettors is fairly common under conditions of high humidity and cool ambient temperatures. It often has the effect of causing

stalling or rough running during warm-up of the engine, and can interfere with performance and fuel economy even when the engine is fully warmed up. Car models vary widely in their susceptibility to icing, and many manufacturers take steps such as heating the carburettor or inlet air in order to minimize the problem.

When fuel is vaporized in the carburettor the latent heat effect chills the carburettor and air stream, sometimes by as much as 20°C. The extent of cooling depends on the volatility of the fuel, the volume of the fuel flowing, the temperature around the carburettor and the amount of heat soaking back to the carburettor from the engine. If the inlet air contains sufficient moisture, water will condense on to the cool carburettor parts and will freeze if the temperature is low enough. The weight of water present in air at any fixed level of relative humidity increases with increasing temperature, so that the most critical temperature for icing to occur is a compromise between having an ambient temperature low enough to achieve less than 0°C in the carburettor and having a high enough ambient temperature for the air to contain sufficient water vapour to cause significant ice formation. This is illustrated in Fig. 17 which shows the range of humidity and temperature over which, for a specific model of car, sufficient ice is formed during warm-up to cause stalling.

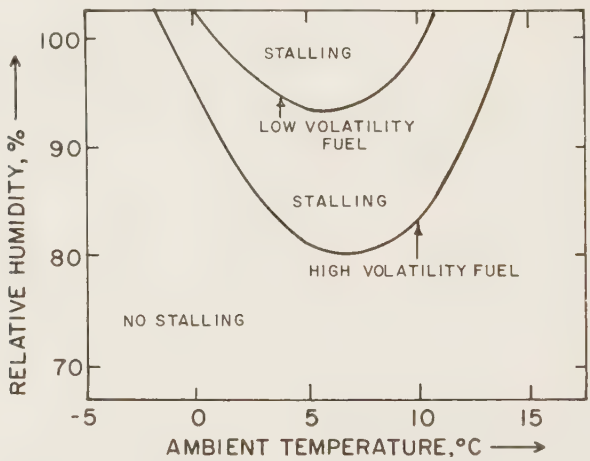

FIG. 17. Influence of ambient temperature, relative humidity, and fuel volatility on carburettor icing.

It is possible, in unusual weather conditions, to get stalling at ambient temperatures well below those at which one would normally expect icing to occur—in ice fog for example, where particles of ice settle directly on the carburettor parts.

Figure 17 also illustrates the general effect of fuel volatility, and shows that increasing the volatility widens the range of both humidity and temperature over which stalling of the car due to icing can occur. Unfortunately it is not possible simply to control the carburettor icing by means of gasoline volatility, since other performance factors such as warm-up and cold start would suffer.

It has been mentioned that icing causes different problems in different cars. In many cases ice formation is most severe on the throttle plate of the

carburettor, and it is this condition which leads to stalling, because when the throttle is closed to the idle position the ridge of ice formed restricts the flow of air past the throttle plate. Stalling can also be caused by heat soak-back to the carburettor turning ice on the throttle plate to slush, which slides into the air passage, again restricting the air flow. This throttle plate type of icing rarely persists when the engine is fully warmed up. A more serious form of icing is when ice builds up on the entry to the venturis and spray elements, thus reducing the effective area of the air passage and causing loss of power and poor fuel consumption. This type of icing occurs with fully warmed-up engines and is most prevalent under motorway driving conditions for those cars susceptible to it. In severe cases it can cause the engine to stop completely, and under these circumstances, after a few minutes to allow heat soak-back to melt the ice, the car can be restarted normally. Icing can also significantly increase emissions of carbon monoxide and hydrocarbons from the engine, since the fuel/air ratio is increased.

Control of icing so far as the fuel is concerned is effected by a combination of volatility and use of anti-icing additives. For most cars the fuel volatility parameter that correlates best with icing tendency is the 50 per cent evaporated temperature, but there are restrictions in the range over which this parameter can be controlled without upsetting other gasoline characteristics. Anti-icing additives are therefore a valuable aid to ensuring trouble-free operation. Two types of additives are used—cryoscopic and surfactant. The cryoscopic additives function by depressing the freezing point of the condensed water so that it does not turn to ice. Alcohols such as ethanol or iso-propanol have been used as cryoscopic additives, although a more effective range of materials are the glycols such as hexylene glycol or dipropylene glycol. One problem encountered with cryoscopic additives is their tendency to be leached out into the water bottoms of tanks during storage and transportation.

The second group of anti-icing additives used are the surfactants. These, as the name suggests, are surface-active materials, and they probably function by forming a mono-molecular hydrophobic film over the internal metal surfaces of the carburettor, thereby preventing the adherence of ice crystals, and by modifying, to some extent, the crystal structure of the ice. Hundreds of different materials have been patented for use as surfactant anti-icers amongst which are such compounds as polyalkylene glycols, alkyl phosphates, and alkyl amines. Cryoscopic anti-icers are normally used in the range 0.03 to 1.0 per cent vol, while the surfactant additives are used at levels of 30 to 150 p.p.m.

Procedures for measuring carburettor icing have been developed by the British Technical Council[14] and include tests for both idle and cruise icing. The procedures when operated on a dynamometer in a climatic chamber, use a fixed temperature (5°C) and humidity (95 per cent Relative Humidity), and involve assessing the degree of malfunction that occurs. They can be used for comparing the relative susceptibility of car models or intake heating systems to carburettor icing, as well as for evaluating the effectiveness of various additives/gasolines in overcoming this problem.

6.8 Influence of Volatility on Fuel Economy

Economy is not simply dependent on the heat content of the fuel; it is also greatly influenced by volatility. For short runs, fast warm-up is vital for good

fuel consumption so that a high mid-fill volatility (i.e. having volatile components in the middle boiling range of the gasoline) is important under these conditions. Carburettor icing in some cars in certain weather conditions can also adversely influence fuel consumption. Engine factors such as air/fuel ratio also play a large part, as discussed in some detail in the section on combustion (Section 5). Evaporation losses, as mentioned earlier, can also have a small effect.

A high specific gravity fuel will contain more energy per gallon and generally have a lower volatility than a low specific gravity fuel. The heavy hydrocarbons that give a high heat content per gallon are the aromatics found mainly in catalytic reformates, and it can readily be demonstrated that a high percentage of such components will improve economy under steady running conditions. Too great a proportion of the higher boiling components can give rise to other problems such as crankcase dilution and deposit formation (discussed later), as well as worsening mixture distribution between cylinders.

It is difficult to summarize briefly the complex question of fuel economy, but it is generally true to say that a compromise has to be made between high mid-fill volatility (for good mixture distribution and quick warm-up) for short-trip operations, and low mid-fill and heavy-end volatility (for maximum heat content) for long-trip operations.

6.9 Crankcase Oil Dilution and Engine Deposits

Some of the benefits and debits of decreasing mid-fill and heavy-end volatility have been mentioned above. At the heaviest end of the gasoline volatility range, as controlled by the 90 per cent distillation temperature and final boiling point, crankcase oil dilution can be a problem. This causes lubricants to be washed from the cylinder walls whenever gasoline reaches the cylinder in liquid form, and the high-boiling part of the fuel, together with condensed partly-burned fuel vapours, can find their way past the piston rings into the crankcase. When frequent cold starts with prolonged choke operations are made, very significant dilution of the lubricant, up to about 10 per cent, can occur. Excessive dilution reduces the oil viscosity and upsets its lubrication efficiency, although it can also be a marginal benefit in helping cold starting. However, modern engines tend to warm up quickly and have smaller oil and coolant capacities than engines of 20 years ago, so that most of the diluent is quickly evaporated as the oil reaches its working temperature. Gasolines today generally have their heavy-end volatility restricted to a maximum of about 210°C as measured by the final boiling points, and rarely cause a problem.

The heavy ends of the fuel also tend to be more difficult to burn completely in the cylinder, and are therefore responsible to a large extent for carbonaceous deposits in the combustion chamber leading to increased octane requirements, and on the spark plug giving rise to misfire. These partly burned materials also contribute to deposits in the inlet system and to sludge formation in the lubricant.

7 STABILITY

Motor fuels are often stored for periods of six months or more before they are used. It is essential, therefore, that they do not undergo any deleterious change

under storage conditions. It is also necessary that they remain stable during their passage from the fuel tank of a car to the combustion chamber of the engine so that no harmful deposits are laid down in the inlet system and on the inlet valves. In storage, gasoline is exposed to the action of air at ambient temperature, and during its passage from the fuel tank to the combustion chamber it is again mixed with air, and in the latter case subject also to the effects of heat. An unstable gasoline will undergo oxidation/polymerization reactions under these conditions, forming what is known as gum. This is a resinous material which in the early stages of formation, may remain in solution in the gasoline, but later further chemical changes may cause it to precipitate from solution. It is formed from the olefinic material present which, because of its unsaturated character is more reactive than the other constituents, and the chemical action is accelerated by the action of light and heat. It appears to be a chain reaction initiated by the formation of peroxides and then catalysed by the presence of metals, particularly copper, which may be picked up during refining and handling operations, and in car fuel systems. In this reaction, various trace materials in the gasoline itself may play a part, and contaminants such as polysulphides, thiophenols, and nitrogen compounds are particularly detrimental.

If the fuel contains highly polymerized gummy material it will tend to throw out the deposits early in the inlet system, while less developed gum precursors will not give deposits until further into the system. The point of deposition depends on the time taken to traverse the manifold and the temperature levels encountered. Volatility will also have some influence and as this increases, deposits tend to form earlier in the system. The operation of the engine under constant high-duty conditions tends to favour the formation of lacquer on the inlet manifolds and inlet valves, while low-duty driving lessens this tendency. Engine design also plays a very large part as shown by the fact that some cars are very susceptible to deposit formation in carburettors, inlet manifolds and on inlet valves while others are not.

Additives are available which can reduce such deposit formation in inlet systems and these are discussed in Section 8.

The first steps to improve the stability of motor fuels must obviously be taken in the refinery, and there are various processes available for removing the contaminants or converting them into harmless compounds. When this has been done, deterioration can be prevented by the use of anti-oxidant additives known as inhibitors, which will retard the oxidation of the olefinic constituents. Most of the commercially available inhibitors are phenols or amino compounds. Amounts ranging from 0.001 to 0.02 per cent are usually sufficient to ensure good storage stability. Several theories have been advanced on the mode of action of oxidation inhibitors. One of the more widely accepted explanations is that the oxidation of the olefins in a gasoline is a chain reaction, and that the chain is interrupted by the inhibitor molecules. Another type of additive often used to increase the stability of motor gasolines is the metal deactivator. As stated above, metals, particularly copper, catalyse the reactions producing gum. A metal deactivator can act either by passivation of the metal surfaces, thus preventing gasoline from dissolving the metal, or by the deactivation of metal compounds already dissolved in the fuel. Many of the commercial deactivators contain diamine groups which combine with the

metal to form a compound that does not ionize and has no catalytic action.

Determination of the stability of motor fuels is usually made by the so-called gum tests. The existent gum test is claimed to measure the amount of gum or gum-forming compounds existing in the fuel, while the potential gum test attempts to predict the tendency to form gum on storage and use. These gum tests are usually used as refinery control methods, but are unrealistic as performance criteria in engines. For this reason engine tests have been developed to examine gasoline for its tendency to form deposits in inlet systems. Apart from gum tests, measurement of trace compounds known to promote instability has been attempted in an endeavour to relate their presence with the stability, or otherwise, of the gasoline. It is most desirable that these active compounds, which adversely affect stability, should be removed to safe limits by suitable refining.

A further effect that has been noticed in recent years is the influence of oxidized gasoline on elastomers. The presence of hydroperoxides, particularly in the presence of metal ions such as copper, cause some elastomers to harden and become brittle, and others to become soft and unserviceable. Although the use of anti-oxidants and metal deactivators avoids these problems to some extent, the proper selection of suitable materials for fuel lines, etc. and the avoidance of the use of copper in the fuel system are the most effective way to eliminate this problem.

8 GASOLINE ADDITIVES

Additives are used in gasoline for two main reasons. The first is to help ensure the satisfactory performance of engines (e.g. by minimizing deposits in carburettors, on valves, etc.), and the second is by supplementing refinery processing (e.g. by the use of anti-knock agents and anti-oxidants). Many of the additives used have already been discussed elsewhere in this chapter and the information is summarized in Table V.

Other additives that can be used in gasoline are:

Detergents and dispersants

These are used to minimize deposits in the fuel intake system (particularly in the carburettor) and also, to some extent, to supplement the sludge dispersant quality of the lubricant.

Carburettor deposits normally consist of gum-like materials arising from the oxidation and polymerization of some of the less stable gasoline components. The use of anti-oxidants and metal deactivators, of course, plays some part in improving gasoline stability and hence in reducing this type of deposit formation. Carbonaceous particles arising from combustion can find their way into the carburettor and cause deposits by means of exhaust gas recycle (not common in UK), i.e. PCV (Positive Crank-case Ventilation) systems which lead fumes from the crankcase back into the induction system, and to a small extent, by valve overlap.

Deposits round the throttle plate area can upset fuel/air ratios at idle, leading in some cases to rough engine operation, increased hydrocarbon and carbon

TABLE V

Additive	Function	Composition	Refer to section
Anti-knock compounds	To improve octane quality	Lead alkyls such as tetramethyl lead Methylcyclopentadienyl manganese tricarbonyl	5.2
Anti-icing additives	To minimize engine stalling and power loss due to ice formation in carburettors and fuel lines	Freezing point depressants such as alcohols and glycols Surfactants such as derivatives of phosphoric acids and amines	6.7
Anti-oxidants	To minimize gum formation and improve storage stability	Phenylene diamine and alkyl phenol compounds	7
Metal deactivators	To prevent catalysis of oxidation processes by deactivating metal ions such as copper	Example is: *N,N*-disalicylidene 1,2 propanediamine	7
Combustion chamber deposit modifiers	To minimize misfire due to lead fouling of spark plugs and to reduce surface ignition and preignition	Organophosphorus compounds Not now widely used	5.4

monoxide emissions and, in low-speed urban type driving, somewhat reduced fuel economy. Surfactant additives can keep many parts of the carburettor clean by detergent action. The types of surfactant compound that are used for this purpose are usually polymeric, and can be amines and derivatives of carboxylic and phosphoric acids.

Some of these materials can also minimize deposits in the manifold and on the underside of inlet valves, although, it must also be said, some of the earlier additives could actually worsen valve deposits. Often solvent oils (see below) are used in combination with detergent/dispersant additives in order to ensure that the inlet valve tulips are kept clean.

A certain proportion of these additives appears to survive the combustion process, particularly during choke operation, and find its way past the piston rings and into the lubricant. By this route the additives are able to enhance the sludge dispersant qualities of the lubricant. Clearly this is of most value when lubricants having low dispersant levels are used, since modern high-quality lubricants already have adequate sludge dispersant properties. However, there may be some value in the constant 'topping up' of the dispersant level in the lubricant.

Anti-corrosion additives

Rust can be a problem in car fuel systems, since it can plug filters and block carburettor jets. In the engine itself rust on bores and rings, arising from the corrosive products of combustion, can increase wear rates. The use of certain surface-active chemicals helps to overcome rust problems in the engine and in gasoline distribution systems, e.g. in bulk tankage, sea and road tankers, pipelines, etc.

Anti-wear additives

Anti-wear additives in gasoline, as would be expected, are most effective in controlling wear in the areas which which the gasoline comes into contact, i.e. the upper cylinder bore and piston rings. They can, however, also function in the same way as dispersant additives by finding their way past the piston rings into the lubricant, thus enhancing its overall anti-wear properties. The latter aspect is, however, a minor one with modern lubricants whose prime purpose is to overcome wear. In the cylinder bore, however, the lubricant can drain away when the engine is stopped, and the corrosive products of combustion can eat into the cylinder walls and piston rings, thereby increasing wear rates. The use of anti-corrosion additives reduces corrosive wear, since when an engine is switched off it continues to revolve for a few cycles, thus inducing unburnt gasoline, containing additive, into the cylinder. Mechanical wear can be reduced by the use of upper cylinder lubricants which are light lubricating oils sometimes added to gasolines in amounts up to one half per cent. Some phosphorus compounds and a number of other chemicals are known to have some effect in reducing mechanical wear and can also be used in gasoline.

9 FUEL ECONOMY

Since the 1973 war in the Middle East with the subsequent price increases in crude oil, the importance of fuel economy has increased rapidly. The following

summarizes briefly the gasoline quality aspects that can influence fuel economy and which have already been discussed.

Specific gravity of hydrocarbon fuels

There is a direct relationship between fuel density and its volumetric heating value and hence between specific gravity and relative fuel economy. It has been estimated[18] that under long-trip road conditions an increase in specific gravity of 0.1 can give a fuel economy benefit of 7.5 to 8 per cent.

Octane quality

In most cases this has only an indirect effect on fuel economy in that the higher the octane quality available, the higher the compression ratio that a manufacturer can use and hence the lower the fuel consumption. However, for cars fitted with knock sensors, the octane requirement of the engine is reduced when knock is detected and this can result in a lower power output. In such cases fuel consumption is increased if the same speed is maintained.

Volatility

Fuels which give a quick start and a fast warm-up yield improved fuel economy for short-trip operation. Such fuels have a relatively high volatility, and hence also tend to be more susceptible to carburettor icing (unless an anti-icing additive is used). Long-trip economy is achieved by having a high proportion of heavy hydrocarbons in the fuel.

Anti-icing effectiveness

Ice in the carburettor can upset fuel/air ratios and dramatically increase fuel consumption. However, it must be pointed out that carburettor icing conditions occur only for limited periods, and that the intake air heating system on most modern cars makes them less prone to this problem than vehicles of a few years ago. The use of additives and, to a lesser extent, restrictions on volatility, control this problem.

Carburettor detergency

The use of carburettor detergents can help to maintain a carburettor free from deposits, and hence enable design levels of air/fuel ratio to be maintained. Normally deposits in carburettors only adversely influence fuel economy under conditions of low throttle opening, i.e. when the vehicle is idling or cruising at low speed under a low load. These additives, therefore, can normally show only a limited economy benefit.

Anti-misfire quality

Lead can give rise to deposits on plugs which, in relatively extreme cases, can cause misfire and hence a worsening of fuel economy. It is rarely a problem in

modern cars and can be overcome by reduced lead levels or the use of an anti-misfire additive.

Viscosity

The range of viscosity found in most commercial gasolines has no significant influence on fuel economy, but if polymeric additives were ever used to thicken a gasoline outside its normal range, then leaner air/fuel ratios than design could be achieved. This would generally have the effect of improving fuel economy, but probably at the expense of driveability.

10 GASOLINE SPECIFICATIONS

Gasoline quality is controlled first by National specifications (in countries where such specifications exist) and secondly by specifications set up within

TABLE VI
BS 4040 Motor Gasoline Specification

Grade	RON	MON
5 Star*	100 minimum	86 minimum
4 Star	97 minimum	86 minimum
3 Star	94 minimum	82 minimum
2 Star	90 minimum	80 minimum

* The 5 star grade is no longer available in the UK.

TABLE VII
General Requirement for all Grades of Petrol

Property	Limit		Test method	
	Min	Max	BS reference	Technically equivalent to
Water and suspended matter	—	None visible	—	—
Distillation				
Distillate evaporated at 70°C, % (v/v)	10	45	4349†	IP 123/78
Distillate evaporated at 100°C, % (v/v)	36	70		
Distillate evaporated at 180°C, % (v/v)	90	—		
Final boiling point, °C	—	220		
Residue, % (v/v)	—	2		
Copper corrosion, 3 h at 50°C	—	class 1	4351†	IP 154/78
Sulphur content, % (m/m)	—	0.2	4350	IP 107/73
Existent gum (solvent washed), mg/100 ml	—	5	4348	IP 131/77
Oxidation stability, min.	240	—	4347	IP 40/74
Lead content, g/l	0.05	0.40*	5657	ASTM D3341.74

* Scheduled for reduction to 0.15 g/l by 1986.
† Under revision—see BS 4040.

each oil company. The UK National specification (BS 4040) provides an indication to the retail purchaser of the relative anti-knock quality of gasoline on the market (Table VI) and also lays down minimum standards for other properties.

The internal specifications set by each oil company in general exceed minimum National specification levels. The size of the margin is set to provide the desired level of market satisfaction.

A number of specifications for reference gasolines have been established by the British Technical Council[15] for reference testing and for engine development. Each fuel represents a relatively severe or extreme example of gasolines that are commercially available. The following BTC reference fuels are currently available (1982).

RF-24 to 29—High and low octane fuels for anti-knock tests
RF-40 to 42—Leaded fuels for volatility tests
RF-43 to 48—Unleaded fuels for volatility tests

11 NEW GASOLINE BLEND COMPONENTS

Each stepwise reduction in lead, as a result of legislation to minimize lead in the atmosphere, requires additional processing severity and, in many cases, capital investment for new processing facilities, if octane levels are to be maintained. The increase in crude prices since 1973 has meant that certain chemical compounds having good octane quality may now be competitive with high-octane petroleum streams and their use may avoid costly new facilities.

These compounds have been designated here as blend components rather than additives, since they are normally used in the range 3 to 15 per cent instead of the several hundred parts per million that is typical of lead.

The most commonly used materials are oxygenates and these fall into two classes—alcohols and ethers.

Alcohols Methanol, ethanol, isopropanol, and tertiary butanol are well known as gasoline blendstocks and all have excellent research octane qualities as shown in Table VIII.[16] However, the motor octane levels are such that the sensitivities (RON–MON) for methanol and ethanol are large, and for isopropanol and tertiary butanol are moderately high. For this and other

TABLE VIII
Octane Values of Oxygenates

	Determined		Typical blend values	
	RON	MON	RON	MON
Methanol	114	95	130	103
Ethanol	111	94	120	106
Isopropanol	106	99	—	—
Tertiary butanol (TBA)	113	110	108	98
Methyl *t*-butyl ether (MTBE)	117	101	115	104
t-Amyl methyl ether (TAME)	112	99	111	100

reasons, cars on the road may be more prone to knock on alcohol-containing fuels versus conventional fuels of the same RON.

The physical properties of the alcohols are summarized in Table IX[16] and from this it will be seen that, compared with a typical gasoline, there are some very significant differences. Thus they have higher specific gravities, lower vapour pressures, are soluble in water, have lower stoichiometric air/fuel ratios and heats of combustion, and higher heats of vaporization. As the molecular weight of the alcohols increases, so they become closer to gasoline in most respects.

TABLE IX
Physical Properties of Oxygenates

	Methanol	Ethanol	Iso propanol	TBA	MTBE	TAME	Gasoline
Specific gravity, 60/60°F	0.796	0.794	0.789	0.791	0.746	0.770	0.720/0.780
Reid vapour pressure, bars	0.35	0.16	0.13	0.14	0.61	0.22	0.75
Boiling point, °C	65	78	82	83	55	86	20/200
Solubility of water	Miscible	Miscible	Miscible	Miscible	1.4%	0.6%	200p.p.m.
Stoichiometric A/F ratio	6.5:1	9.0:1	10.3:1	11.1:1	11.7:1	11.9:1	14.7:1
Nett heat of combustion, Kcal/kg	4767	6624	7256	7827	8400	9000	10200
Heat of vaporization, Kcal/kg	276	218	177	143	77	78	43
Flash point, °C	11	13	12	11	—	—	−43
Limits of flammability							
% vol lower	6.7	4.3	2.0	2.4	—	—	1.4
% vol higher	36.0	19.0	12.0	8.0	—	—	7.6
Melting point, °C	—			25		–	–

The differences give rise to a number of serious problems and effectively limit the amount of alcohol that can be used in motor gasoline, unless it is to be used only in specially modified vehicles.

The lower stoichiometric air/fuel ratio means that the mixture with such fuels is leaner and the car which has not had adjustment of the carburation may therefore be more prone to driveability problems. The lower heat content of alcohols, even on a volumetric basis, indicates poorer fuel economy. Although the RVPs of pure alcohol are lower than that of gasoline, when alcohols are blended into conventional gasolines, the RVP is increased very considerably, particularly for methanol and ethanol. In addition, because of azeotrope formation, the distillation curve of the gasoline is dramatically changed. Here the lower alcohols again have the greatest effect, and 5 per cent methanol can increase the percentage evaporated at 70°C by as much as 15 per cent. Although methanol and ethanol give a substantial increase in front-end volatility when they are added to gasoline, the effect on vapour-locking tendency is less than expected due to the higher latent heat of evaporation of the alcohols. Of course, in practice, blends would be made to meet given specifications and this could mean, particularly for the lower alcohols, that less

butane could be incorporated into the blend. In some cases this could represent a significant economic penalty for the refiner.

Further problems that can arise from the use of alcohols are due to their solubility in water. Thus high losses to water bottoms can occur during storage and distribution; there can be a greater amount of water dissolved in the gasoline itself and this, in turn, can lead to increased corrosivity. Quite a small amount of water can cause separation into two phases unless higher alcohols such as TBA are present. Haze can also be a problem when relatively high concentrations (more than 5 per cent) of TBA are used.

The lower alcohols in particular can attack various components in the fuel system. Methanol is reported to attack aluminium, copper, zinc, lead, and magnesium. Alcohols are strong solvents and adversely affect certain elastomers, rubbers, and plastics used in the fuel system. In some cases they cause swelling and softening, and in others they make the elastomer hard and brittle by extracting the plasticizer.

Ethers The most common ether in use is methyl tertiary butyl ether (MTBE), although tertiary amyl methyl ether (TAME) and di-isopropyl ether (DIPE) have also been suggested as suitable gasoline blend components. Octane data and information on the physical characteristics for MTBE and TAME have been included in Tables VIII and IX. It will be seen that they have excellent RON levels and they are better than the alcohols in terms of their influence on sensitivity. Their physical properties are also very much closer to conventional gasolines than the alcohols, and since they do not show a high polarity and solubility in water, the adverse effects shown by alcohols are very much less apparent. Overall MTBE appears to be relatively trouble-free high-octane blend component that has little effect on volatility.

12 ALTERNATIVE MOTOR FUELS

12.1 Liquefied Petroleum Gas (LPG)

LPG consists essentially of C_3 and C_4 hydrocarbons and is readily available directly from crude oil distillation and from cracking and other processes. Its use as a motor fuel is already established and its importance relative to gasoline is controlled largely by the rate of tax applied to it. For this reason in some countries it is used very widely and in others the incentive is so low that its use is negligible.

LPG has a number of advantages over liquid fuels. It mixes more readily with air and so gives a better mixture distribution. It can, for this reason, be used at somewhat leaner air/fuel ratios and this can give lower carbon monoxide and hydrocarbon exhaust emissions. LPG burns more cleanly than gasoline and hence gives rise to less combustion chamber deposits. It has excellent anti-knock performance, provided that unsaturates are not present in excessive proportions, and it is resistant to preignition. It gives excellent cold-start and warm-up performance.

There are, however, a number of disadvantages. Arranging for LPG to be readily available is difficult because of storage and distribution problems—it must be stored and transported in tanks capable of withstanding quite high

pressures. On the vehicle itself the LPG tank is quite bulky, particularly since the volumetric economy of LPG is not as good as a liquid hydrocarbon fuel. The performance of LPG in terms of emissions, power, and economy is very dependent on composition, i.e. on the C_3/C_4 ratio and on the level of unsaturates since these strongly influence stoichiometry. It is essential, therefore, that within any one geographical region the composition of LPG for automotive use is adequately defined and that all manufacturers make a similar product. In addition, although the saturated hydrocarbons have excellent anti-knock quality, some of the unsaturates have a relatively poor motor octane number and are susceptible therefore to causing high-speed knock.

For passenger vehicles in the UK it is most common to have a dual fuel system of LPG/gasoline in order to overcome the problem of restricted availability. There are, however, some specialized vehicles that use LPG as the sole fuel, e.g. fork-lift trucks that operate in warehouses and enclosed spaces where it is necessary to minimize carbon monoxide emissions.

12.2 Alcohols

The use of alcohols as blend components has already been discussed, but there is increasing interest in the use of neat methanol and ethanol as alternatives to gasoline. This is in spite of their generally high cost relative to gasoline and is due mainly to the following reasons:

1. To enable countries that are short of oil to have a secure domestic source of fuel. Methanol can readily be made from coal, wood or cellulosic wastes and ethanol either synthetically or by fermentation.
2. To create a market for surplus farm products.
3. To satisfy ecological and environmental preferences for a fuel that is derived largely from renewable resources and which does not require the use of lead anti-knock compounds.

Methanol and ethanol differ very markedly from gasoline, and Tables VIII and IX summarize the most important of these differences, which must be taken into account when designing a vehicle to operate satisfactorily on alcohol fuels. The main adverse influences are:

Cold startability The combination of the higher heat of vaporization, higher minimum flammability limits and the lower vapour pressures all conspire to make cold starting more difficult. This can be overcome by fuel preheating devices and/or by blending small amounts (5 to 10 per cent) of light hydrocarbons or gasoline into the alcohol.

Driveability The same characteristics that give rise to poor startability also lead to unsatisfactory driveability unless the induction system of the vehicle is modified.

Volumetric fuel consumption The advantageous anti-knock quality of the alcohols means that higher compression ratios can be used, with the consequent improvement in thermal efficiency. Unfortunately this is more than offset by the lower volumetric energy content of the alcohols (49 per cent for methanol

and 66 per cent for ethanol as compared with gasoline), and it has been estimated[17] that for a car optimized for use on methanol, the volume of fuel consumed over a set distance is 60 per cent greater than with gasoline. This, in turn, requires larger fuel tanks which would again provide an economy debit.

Compatibility with fuel system materials Alcohols containing some water are highly corrosive, not only to ferrous metals but also to some non-ferrous metals such as magnesium and terne plate (a lead/tin alloy used for coating steel fuel tanks). Anti-corrosion additives are normally necessary with such fuels. In addition many non-metallic materials (e.g. elastomers, plastics, rubber, etc.) used in fuel systems are adversely affected. Some swell excessively while others shrink and harden.

Other problems The high toxicity of methanol means that special care is needed in designing the fuel system. The use of ethanol gives rise to a special problem in that it is necessary to add denaturing agents to prevent potable ethanol from being extracted from the fuel.

Both alcohols provide a special hazard in that their flames are barely visible.

Finally, the solubility of alcohols in water means that it is necessary to keep the distribution system as dry as possible.

12.3 Synfuels

These are derived from natural materials and are composed of hydrocarbons of mostly similar types to those found in conventional gasolines. The real difference is the more complex recovery and processing operations that are required to turn the raw materials into satisfactory gasolines.

Two of the types of material involved are Athabasca tar sand and oil shale deposits, and these pose different problems for economically obtaining oil. Tar sands contain what is extremely viscous crude oil, which has to be separated from the sands by physical means and converted to more usable materials, chemically the same as those derived from conventional crude oils. Oil shales contain large amounts of complex organic solids (kerogen), which on strong heating break down to give, among other products, shale oil. Raw shale oil liquids, however, are highly olefinic and have a high nitrogen content. The naphtha fraction, even after extensive hydroprocessing, makes a poor gasoline blendstock.

Coal is also used to produce synfuel, and two basic methods are possible. There is a synthetic route, commercial in South Africa, in which the coal is gasified by the Lurgi process to produce synthesis gas (carbon monoxide and hydrogen) which is then recombined by a Fischer-Tropsch synthesis to produce hydrocarbons for gasoline blending. Alternatively the coal can be subjected to pyrolysis or solvent extraction (with or without the use of hydrogen) to produce hydrogen-rich products. The latter process is not yet in commercial operation.

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21

Diesel Fuels

By J. H. BODDY

The diesel engine has now extended over a much wider range of applications than any other engines currently in use. Within the past eighty years diesel engines have been used wherever engine power has been required. They are found driving small and large electric power generating and pumping units; in the main propulsion of ships and their auxiliaries; in large and small road vehicles; they are used for off road agricultural and civil engineering vehicles and machinery and also for railway locomotives. Whilst few examples now exist, diesel engines usually power the lighter than air airships and in the past have seen application in winged aircraft. They find no favour today for this latter purpose because other engine types have far higher power to weight ratios. It must also be said that diesel engines are not unique to any one part of the world. They will be found everywhere where man needs to augment his own work capability. Therefore, diesel fuels have a universal market.

The power producing capabilities of diesel engines vary from 1 or 2 kW to about 20 000 kW and may be used for stand-by or continuous duty, so that individual units may vary in annual fuel consumption from a few hundred litres to many thousand tonnes. Although diesel engines are regarded, justifiably, as the most rugged and reliable of engines, maintenance is necessary and the extent of the maintenance needed may depend in part on the quality of fuel used. There are instances where maintenance needs must be minimal and this is achieved at some economic cost, by using selected highly refined fuel, but in general diesel engines will find most favour where operating economy in terms of fuel cost is paramount. In recognition of this interest many designs aim to be relatively insensitive to fuel quality and indeed, within the scope of petroleum fuels diesel engines have operated over the range from gasoline to neat crude oil. Whilst this wide range of adaptability does exist it has to be recognized that it is not inherent in any one engine type to be so omnivorous. Detailed design changes are necessary to utilize all petroleum fuels and if, as is projected for the future, fuels are extended to coal and vegetable oils, then even wider variants of the basic design must be contemplated.

It does become apparent that the wide variety of fuels that might be designated diesel fuels would have other uses, for example as fuels for boilers or gas turbines. In accepting multiple roles for fuel products and at the same time providing a consistency of performance for one or other of these multiple roles, special properties may need to be limited for one role which are not necessary for the others. In the course of this chapter a broad look will be taken at petroleum products and other materials used as diesel engine fuels and the good and not so good properties for this particular purpose identified.

THE DIESEL ENGINE

Before embarking on the characterization of diesel fuels some description of the engine is necessary, but can only be somewhat cursory within the bounds of this chapter. Nevertheless this should be sufficient to draw attention to the critical fuel properties.

Like the petrol engine the diesel is a reciprocating internal combustion engine, but differs in a fundamental respect: the air intake to the engine cylinder is unthrottled and not premixed with fuel. Furthermore, ignition is achieved spontaneously without the aid of a sparking plug. Air induced into the cylinder at atmospheric pressure is compressed to a volume ratio somewhere near to 1:16, but it could be a few ratios less, or more, as determined by design features, such as engine speed and application and the fuel expected to be used. At the end of compression fuel is injected into the cylinder, the quantity injected is limited to control the power from the engine. The mass of air compressed will become heated by the compression according to the fundamental law of thermodynamics $PV/T =$ a constant. The speed of compression and the thermal properties of the cylinder will determine how little heat is lost during the process and, hence, the final temperature reached at the end of the compression stroke, i.e., the value of n in the relationship $PV^n =$ constant. In the event the temperature reached must be high enough for the fuel to ignite spontaneously. In respect to this the nature of the fuel as well as the engine design is critical. A diagrammatic representation of the combustion cycle is shown in Fig. 1. The first stage is the compression of air to a small percentage of its original volume. This increases the pressure many times and the temperature to 500 °C or more. As fuel is injected into this heated and turbulent air for the second stage, mixing takes place and some precombustion oxidation of the fuel occurs before combustion begins. Finally, continuous burning of the incoming fuel from the injector proceeds as the third stage. The sooner ignition

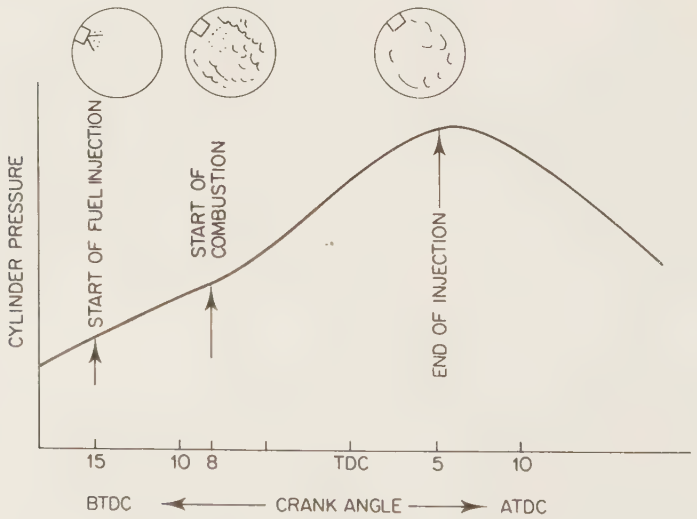

Fig. 1. Diesel cylinder pressure–time diagram.

takes place after injection starts the smoother and quieter will the engine operate. The quality of the fuel is a major factor influencing this delay, but injection quality and mixing will also be significant factors.

Subsequently the pressure rises before and after the piston reaches top dead centre during which time the total chemical energy of the fuel is released as heat to be converted into mechanical energy by the piston movement.

Fuel Properties

It is a general property of hydrocarbons that the more volatile they are the higher the temperature for spontaneous ignition. (Different types of hydrocarbons will have different relationships, but will show the same trend.) It is for this reason that the less volatile middle distillate fractions of petroleum crude and even residues are more readily applicable to diesel engines than gasoline or lighter fractions.

The transfer of a liquid fuel from a tank at atmospheric pressure into the confined space of the engine cylinder where the pressure is some 30 or more bars, necessitates the use of a high pressure pump and injector which release the fuel at the appropriate time. The injector obviously needs to be within the cylinder, or precombustion chamber, so that its temperature must approximate to that of cylinder, or have some positive cooling arrangement which adds sophistication to the engine design. These factors suggest certain important fuel properties which, if not possessed, impose complicated engineering problems. Amongst these properties are: easy pumpability over the range of ambient temperatures and pressures prevailing in the engine working environment; non-corrosivity to metal parts and lubricating properties for assisting the free movement of sliding metallic surfaces in the pump or injector; capability to withstand high temperature without chemical change that might inhibit the flow of fluid or form deposits. The next factor to consider is that fuel directed into the engine cylinder must be in a state which is readily able to burn. This necessitates vaporization which can be best achieved by breaking the fluid up into small droplets and distributing these droplets evenly throughout the air with which they will burn. It must then be volatile under the temperature and pressure conditions prevailing in the engine cylinder. The fuel injector is designed to effect the atomization of the fuel, but can only be effective within a limited range of viscosity of the fuel if excessive pumping pressures involving mechanical losses are to be avoided. In the final stage where the fuel is utilized to produce heat and engine power, the heating value must be adequate and any residue of fuel, or its products of combustion, must not foul, corrode, or erode the cylinder or other component engine parts. When the exhausted combustion products are emitted from the cylinder, through the exhaust valve and exhaust system they should not contain excessive soot particles which might clog the exhaust valves and form smoke and noxious fumes when finally emitted to the atmosphere. Diesel engines used in road vehicles are being subjected to laws which limit the gaseous emissions; carbon monoxide, hydrocarbons, and oxides of nitrogen as well as smoke, as defined by EEC directives, ECE regulations, and UK Government Statutory Instruments.[1,2,3] Interest has also been shown in other emitted substances having possible toxic properties, but not necessarily within the range of concentration that is significant to human health. Amongst

these are sulphate radicals and polycyclic aromatics. Noise is also a property of diesel engines subject to legislative control when generated by certain applications such as road vehicles. Whilst most of the noise will have little, if any, relevance to fuel properties, diesel knock caused by delay in the start of combustion is related to the properties of the fuel and the efficiency of fuel and air mixing. With an unsuitable fuel ignition will only occur spontaneously after a long delay during which a substantial quantity of fuel has been injected. This ignites explosively causing a very sudden rather than a steady rise in pressure and consequently causes rough running of the engine, as well as smoke emission. As already implied, fuels with high spontaneous ignition temperatures will be less satisfactory for diesel engines and will be those more likely to cause diesel knock.

The odour of diesel exhaust gases, as of the fuel itself, can be obnoxious although assessing when such odours are objectionable is difficult and subjective as discussed later. Attempts at quantifying odour have identified some of the partial oxidation and intermediary aromatic decomposition substances as the more objectionable. There are features of engine design, operation, and fuel characteristics which may be influential.

Fuel Specifications

Over a number of years various standardizing bodies have identified key properties of fuels for specific purposes and thus established standard fuel specifications. To a very large extent these categories of fuels have been related as much to the way in which crude petroleum is distilled and divided up into various fractions as to the particular demands of the consuming device. ASTM have, for a long time, numbered fuels, other than gasolines, from 1 to 6 without separately designating diesel fuels.[4] It was only in 1967 that British Standards combined the Engine and Oil Burner fuels into one standard in recognition of the flexibility to use burner fuels as engine fuels. Fuel specifications are not set for all time either by the requirement of the consuming device, or by the producer of the fuel. There is a continuing liaison between the engineer pointing out where he has most difficulty in using a particular fuel product and the fuel refiner through co-operative and independent research looking for relaxations of specific properties which the engineer has demanded. It is important to note that engine design has been directed in two different ways by the need to accommodate different classes of fuels. Clean burning distillate fuels have inspired the design of high speed engines with relatively high power to weight ratio which are suitable for automotive vehicles and mobile machinery. Residual fuels which would impose excessive maintenance problems on high speed engines can be effective in engines operating up to speeds of several hundred r.p.m. without excessive maintenance. Because such engines have necessarily low power to weight ratio they are only suitable for stationary purposes such as non-mobile power generating units and marine applications.

However, it is not only the engineer and the refiner who contend the specification of a fuel, but safety and pollution control authorities. As an example, it might be cited that whilst the limitations of an engine design, modified by such compensation as can be derived from proper lubricating oil

quality, may set a limit to the maximum sulphur content of a fuel, legislation to protect the environment from pollution by sulphur dioxide has overtaken that limit. Considerations such as environmental control in respect to nuisance, human and material hazard, chronic as well as acute health and safety considerations, are becoming ever more significant features of both vehicle and fuel specifications. In turn, such features, particularly sulphur limitation in diesel fuel, make new demands on refinery processing. Thus there is a continuing evolution in both engine and fuel design.

Table I specifies BS 2869 Class A1 and A2 fuels for diesel engines. Table II lists the requirements of burner fuels E to H of BS 2869 which may be used for medium and slow speed large diesel engines as used in power generating installations.

Added in the tables are the critical engine performance characteristics associated with each fuel property.

Two of the recent specification amendments have been of considerable significance in petroleum refining. The first concerns the reduction of sulphur

TABLE I
UK Specifications of Diesel Fuels to BS 2869

Fuel property	Fuel classification A1	Fuel classification A2	Critical engine performance
Viscosity, kinematic at 40°C			
centistokes min	1.5	1.5	Lubricity
max	5.0	5.5	Fuel atomization
Cetane number, min*	50	45	Diesel knock, engine noise, smoke and gaseous emissions
Carbon residue, Ramsbottom % (m/m), on 10% residue, max	0.2	0.2	Injector deposits
Distillation recovery at 350°C (v/v), min	85	85	Vaporization, smoke, gaseous emissions
Flash point, closed, Pensky-Martens, °C, min	55	55	Storage safety
Water content, % (v/v), max	0.05	0.05	Cold temperature operation and filterability
Sediment, % (m/m), max	0.01	0.01	Protection of injector pump, storage stability
Sulphur content, % (m/m), max	0.3	0.5	Engine corrosion, exhaust emissions
Copper corrosion test, max	1	1	Fuel system corrosion
Cold filter plugging point, °C, max			
Summer (Mar./Sept.) inclusive	0	0	Cold temperature operation in automotive vehicles
Winter (Oct./Feb.) inclusive	−9	−9	
Application	Automotive road vehicles	Off road automotive engines and stationary engine applications	

* Calculated cetane index is approximately equal to determined cetane number that does not contain additives to improve the ignition quality. This index may be used as an alternative to cetane number.

TABLE II

UK Specificiation for Burner Fuels to BS 2869

	Fuel Classification						Critical engine performance
	C_2*	D*	E	F	G	H	
Viscosity, kinematic at 40°C							
centistokes min	1.0	1.5	—	—	—	—	Lubricity
max	2.0	5.5	—	—	—	—	Fuel atomization
Viscosity, kinematic at 80°C							
centistokes max	—	—	13.5	35	83	130	Fuel atomization
Carbon residue, Ramsbottom % (m/m), on 10% residue, max	—	0.2	—	—	—	—	Injector deposits
Flash point, closed, Pensky–Martens, °C, min	—	55	66	66	66	66	Storage and handling safety
Water content, % (v/v), max	Free from visible water	0.05	0.5	0.75	1.0	1.0	Cold temperature, good fuel system operation, good filterability
Sediment, % (m/m), max	Free from visible sediment	0.01	0.15	0.25	0.25	0.25	Burner and pump protection, storage stability
Ash, % (m/m), max	—	0.01	0.1	0.15	0.2	0.2	Furnace deposits and corrosion protection
Sulphur content, % (m/m), max	0.20	0.50	3.5	3.5	4.0	4.0	Furnace corrosion and stack emission control
Cold filter plugging point, °C, max							
Summer (Mar./Sept.) inclusive		0					Cold temperature fuel system operation
Winter (Oct./Feb.) inclusive		−9					
Application	Vaporizing burners	Combustion equipment Stationary diesels gas turbines	Combustion equipment requiring pre-heat to varying levels				

* Specifications not fully detailed here.

content in the distillate grades and the necessary widespread introduction of hydrodesulphurization and/or change of crude source. The second, is a change in the cold temperature operating criteria from Cloud Point to Cold Filter Plugging Point which gives greater flexibility for the use of additives for the improvement of flow properties of waxy fuels under cold temperature conditions.

Within the UK specification BS 2869 there is the division into engine and burner fuels. The fuels A1, and A2, are designated engine fuels whilst fuels C to H are designated burner fuels. It is stated in the standard that 'Considerable use is made of burner fuels Classes E to G as fuels for certain oil engines' adding the warning that 'they are not sold with any guarantee of suitability for the purpose and intending users should satisfy themselves by test or consultation with the engine manufacturer that any particular fuel will be suitable for their equipment'. They draw special attention to ash forming constituents. Fuels C and D are distillate burner fuels, the first designed for vaporizing type domestic burners and the second having similar properties to the A2 grade engine fuel, but excluding a cetane number limitation. Both fuels could be used as diesel engine fuels providing there is due regard for the absence of a cetane requirement in both specifications and the poor lubricity which would be afforded by the kerosine type fuel C. Such a fuel could never be recommended and would only be used in dire emergency. The latter limitation may cause rapid deterioration of fuel injection equipment in some diesel engines. The absence of a cetane number specification in the case of fuel D would be inconsequential for the majority of diesel engines, but many fuels manufactured to the C grade specification would cause the majority of diesel engines to knock noisily if not detrimentally to the engine performance. Because the Class A2 and D fuels do not carry the normal tax on road fuels and are specifically marked with both chemical marker and dye they are not available for use on the road by law.

It will be apparent from the specification tables which engine performance characteristics relate to which fuel property; it must, however, be reiterated that engine design will determine how significant the particular fuel property may be.

Ignition Quality

Whilst ignition quality could become increasingly important in high speed automotive diesel engines, it is less relevant in low speed engines as used in large stationary and marine applications. The point may be illustrated by the example given by C. L. Bailey in the previous edition of this book.[6] In a typical stationary high speed diesel engine running at 2000 r.p.m. and full load, fuel injection will commence some 15° of crank angle rotation before top dead centre and end 5° after top dead centre. With a normal distillate diesel fuel of Class A quality combustion will start 8° of crank angle rotation before top dead centre. This represents a delay of 0.6 millisecs in a total injection period of 1.7 millisecs. Hence, in an engine running no faster than 400 r.p.m. and injection taking place over the same crank angle movement there is five times as long for combustion to start within comparable crank angle ignition delays

and consequently far less time for sufficient fuel, that might cause knock, to enter the cylinder before ignition takes place.

Ignition quality is measured in terms of cetane number using an ASTM standard test engine. The test method designated D613 comprises a single cylinder engine with a variable compression ratio combustion pre-chamber. The cetane number of the test fuel is the percentage volume of cetane in α-methyl naphthalene which gives a standard 13° crank angle ignition delay at the same compression ratio as the test fuel. Test procedures designated IP 41A and 41B were developed by the Institute of Petroleum for use with less sophisticated test engines. However, engine tests other than for referee purposes, when the ASTM D 613 method is used, have fallen out of use and it is customary to use a calculation based on mid-boiling point and the API gravity which gives a Cetane Index corresponding very closely with cetane number. Diesel Index, determined from aniline point and API gravity which provides a measure of ignition quality less close to engine cetane numbers than Cetane Index has formerly been commonly used, but is no longer included in BSI Specifications. Neither Cetane Index nor Diesel Index can give valid indications of ignition quality when ignition quality improvers are added to fuels.

Ignition quality improvers

Organic nitrates are additives which can be used to improve the ignition quality of diesel engine fuel. However, it is unusual for engines to be manufactured which do not perform satisfactorily on one or other of the diesel fuels defined by standard diesel fuel specifications and no fuel refiner has yet found it necessary to utilize such means to achieve those standard qualities. Hence, the use of cetane improvers has been largely limited to research and development work. Blue smoke emissions from diesel power boats starting from cold have been reduced by the application of cetane improvers to the air intake in aerosol form preferably at shut down. Ignition quality improvers will also assist low temperature starting, but for this purpose aspiration of ether is almost as effective and can greatly reduce the threshold starting temperature.

Exhaust Emissions

Up to the recent few years there has been concern only about the smoke emission of automotive diesel engines, but as diesel fuel has become an increasing proportion of the total road vehicle fuel, there is valid reason for introducing gaseous emission controls similar to those applying to petrol engines. Hence, according to the United Nations Economic Commission for Europe Regulation 15, Amendment 04, road vehicles of maximum weight not exceeding 3.5 tonnes with diesel engines should be constructed to conform to manufacturing design and production limits for emission of carbon monoxide, oxides of nitrogen, and hydrocarbons as apply to petrol engines.[7] Ratification of this Regulation by EEC Directive and subsequently UK regulation under the Road Traffic Act 1972 (Vehicle Construction and Use Regulation) will make conformity to these limits legally binding.

An ECE regulation for gaseous emission of diesel engines has been agreed for

manufacturing control of the automotive engines for heavy vehicles. Firm UK legislation does also exist for the control of vehicle diesel smoke by type testing of engines used in vehicles. It is illegal for a vehicle, manufactured since October 1972, to be equipped with an engine which has not passed a vehicle type test in which the exhaust smoke has been measured as not exceeding prescribed limits over a range of conditions of increasing power output. The test procedure is prescribed by BS AU 141a and correlates with the similar test procedures defined in ECE Regulation 24 and the European Community Directive 72/306/EEC.[1,8] The Co-ordinating European Council (CEC) of the Motor and Petroleum Industries which is sponsored by the Institute of Petroleum and other national petroleum institutes and associations throughout Europe played a prominent role in developing both the gaseous and smoke tests defined by the ECE and European Community and standardizes the reference fuels for carrying out the tests. These test procedures apply essentially to the design of the vehicles which must carry a plate indicating that the test has been passed.

Whilst several procedures have been tried, and are used in some countries, to check vehicles for smoke emission on the road, none have been accepted by the UK Government as satisfactory, or better than the subjective observation of smoke density by Government Inspectors on the roadside. These inspectors may order vehicles to be taken off the road and to be tested at prescribed testing stations where full scale tests of the vehicles under load can be made.[9]

Whilst the emission of sulphur dioxide from vehicles is not controlled by vehicle design there is indirect control by limitation on the sulphur content of fuel used in both road vehicles and off road or stationary diesel engines. In conformity with the EEC Directive 75/716 Statutory Instruments Nos 1988 and 1989 of 1976 under the 'Control of Pollution Act 1974' limit the sulphur content of fuels for road and non-road use respectively to 0.3 and 0.5 per cent by weight.[10]

Fuel characteristics that may affect gaseous emissions and smoke are cetane number, sulphur content, distillation characteristics, and density. However, within the bounds of the fuel specification and the errors of the test method the effects are small. Adequate data to define the independent effect of these variables have not been produced. Other than sulphur content it is unlikely that the adjustment of the properties of petroleum products designed as diesel engine fuels will be useful for effecting control of vehicle emissions. However, the advent of non-petroleum fuels such as alcohols and coal derivatives finding use as alternative and/or supplements to petroleum products may make the fuel specification a more prominent factor in vehicle emission control at some time in the future.

Odour

Diesel fuel as well as diesel exhaust have odours which some accept as not unpleasant but which others find objectionable. Objection to the odour of the fuel itself is readily overcome by avoidance of spillage and leaks in fuel systems. Attempts at masking the odour of diesel fuel have not been successful. In so far as the unpleasantness of an odour may be a warning of some hazard, this masking of odours cannot be regarded as beneficial and is a practice to be

discouraged rather than encouraged. Degobert's study of diesel odours examines the various techniques for measurement of diesel exhaust odours by human sensory assessors as well as physico-chemical analysis procedures.[11] Because of the possible hazard to sensory assessors most emphasis in future must be given to the instrumental methods amongst which the liquid chromatograph procedure, originally developed by A. D. Little, is the most promising. The European adaptation of A. D. Little's procedure which assesses the quantities of liquid chromatograph oxygenates and liquid chromatograph aromatics in the exhaust, together with light aldehydes, is not considered fully satisfactory and should also include a component to represent the SO_2 emission. Determining the proper balance of these factors to be representative of what the majority object to, is a problem which has as yet defied solution.

Water sediment, and ash content

The most significant properties of residual fuels for diesel engines are water content, sediment, and ash content. Water is not harmful if homogenized in the fuel in low concentrations; it can, however, present problems when 'slugs' of water clog filters or interfere with the proper functioning of preheaters in fuel lines. It has become common practice to use centrifuges for separating water and sediment from the fuel, but care must be taken to ensure proper temperature control to keep the fuel density lighter than the water phase when the fuel and water have similar specific gravities. Any solid matter must be removed and this can be effected by the centrifuge. It has been a matter of debate what size limit of particle should be removed to minimize wear of fuel injection equipment since different engine manufacturers may prescribe different limits. Of greater concern to the engine itself are the ash constituents which produce corrosive and erosive material when burned. Vanadium and sodium levels in the fuel ash are sometimes critical. Engine manufacturers have specified preferred limits that should not be exceeded.

In the process of combustion sulphur contained in the fuel will produce sulphur oxides and will combine with the ash forming constituents to produce sulphates and sulphites. The sulphur oxides in particular can produce acidic corrosion of engine cylinders under cold running conditions. Advances in lubricant technology have reduced this problem to minor proportions and in the slow speed engines fuels with 4 per cent sulphur content can be used without distress.

In the automotive engine operating with a distillate fuel difficulties with ash content do not exist because distillation essentially discards the ash containing material to the residue. Sediment and water content are usually minimal at the point of delivery from refineries although there can be problems in separating water after processing involving contact with steam in which case over-long settling time in tankage may be necessary to achieve a clear fuel normally required by manufacturing specifications. Water contamination subsequent to supply may come about due to improper storage and handling such that water is allowed to enter tankage or to excess ullage when tank breathing leads to a high level of water condensation. Filters and water separators in vehicle fuel systems are necessary to eliminate fuel pump and injector wear, but in badly designed fuel systems they may cause the fuel supply to be interrupted under

cold temperature conditions. A strainer or filter which is in an exposed position on a vehicle will allow any water separated from the fuel to freeze and so inhibit fuel flow. Similar problems can arise due to wax crystallization from the fuel. The design features necessary to minimize this problem are similar to those necessary to combat the problem of wax crystallization under cold temperature conditions as discussed below.

Cold Temperature Properties

Pour point, cloud point, and cold filter plugging point (CFPP)

These properties of fuels for diesel engines and combustion equipment all relate to the performance of fuels under cold temperature conditions and in consequence the ability of engines, or plant, to operate satisfactorily in cold conditions. The cloud point is the test temperature at which visible wax crystals start to form in a fuel under simple laboratory test conditions and has been regarded as the lowest temperature for pumping the fuel and, therefore, for operation of a vehicle. To cover all but the most severe conditions in the United Kingdom $-7°C$ was used as the cloud point specification temperature limit. However, this posed severe restrictions on the manufacture and availability of gas oil and diesel fuel, particularly under refining operations to maximize distillate yield. Work carried out over a number of years involving the development of flow improving additives by additive manufacturers and joint research by both the motor and petroleum industries under the direction of the British Technical Council and the Co-ordinating European Council, has led to a new method of test for determining the specification point which defines a minimum temperature at which the fuel may be filtered. Such a test is more realistic than cloud point in so far as it takes account of the true conditions under which the fuel must operate and permits the use of fuel additives which, whilst having no influence on the cloud point, maintain the wax crystals so small that they will pass through a filter of comparable size to that suitable for protecting engine fuel pumps and injection equipment. The procedure is the Cold Filter Plugging Point test and is fully described in 'Methods for Analysis and Testing'.[12] The maximum value specified for UK winter grade fuel is $-9°C$. As a consequence of this development the cloud point has now been eliminated from British Standard and most other fuels specification standards.

It has to be recognized that winter temperatures in the United Kingdom do on occasions fall below $-9°C$ and there are many other parts of the world where diesel engines are used which experience temperatures much below $-9°C$. The choice of maximum CFPP for the United Kingdom was based on a very high probability of winter temperatures being above $-9°C$ and the small risk of lower temperatures.* Based on past experience this small risk should last for only a short time and has to be accepted if adequate fuel supplies are to be maintained. The low pressure parts of diesel vehicle fuel systems vary in design such that some are more vulnerable to cold weather than others. Figures 2 and 3 taken with permission from a publication by the British Technical Council[13]

* At the Meteorological Office Station recording the coldest extremes of air temperature for a populous region in the UK the risk, based on data over thirty years, was 1 in 650 of a temperature of $-8°C$ or below occurring for a period of more than 8 hours during October to February.

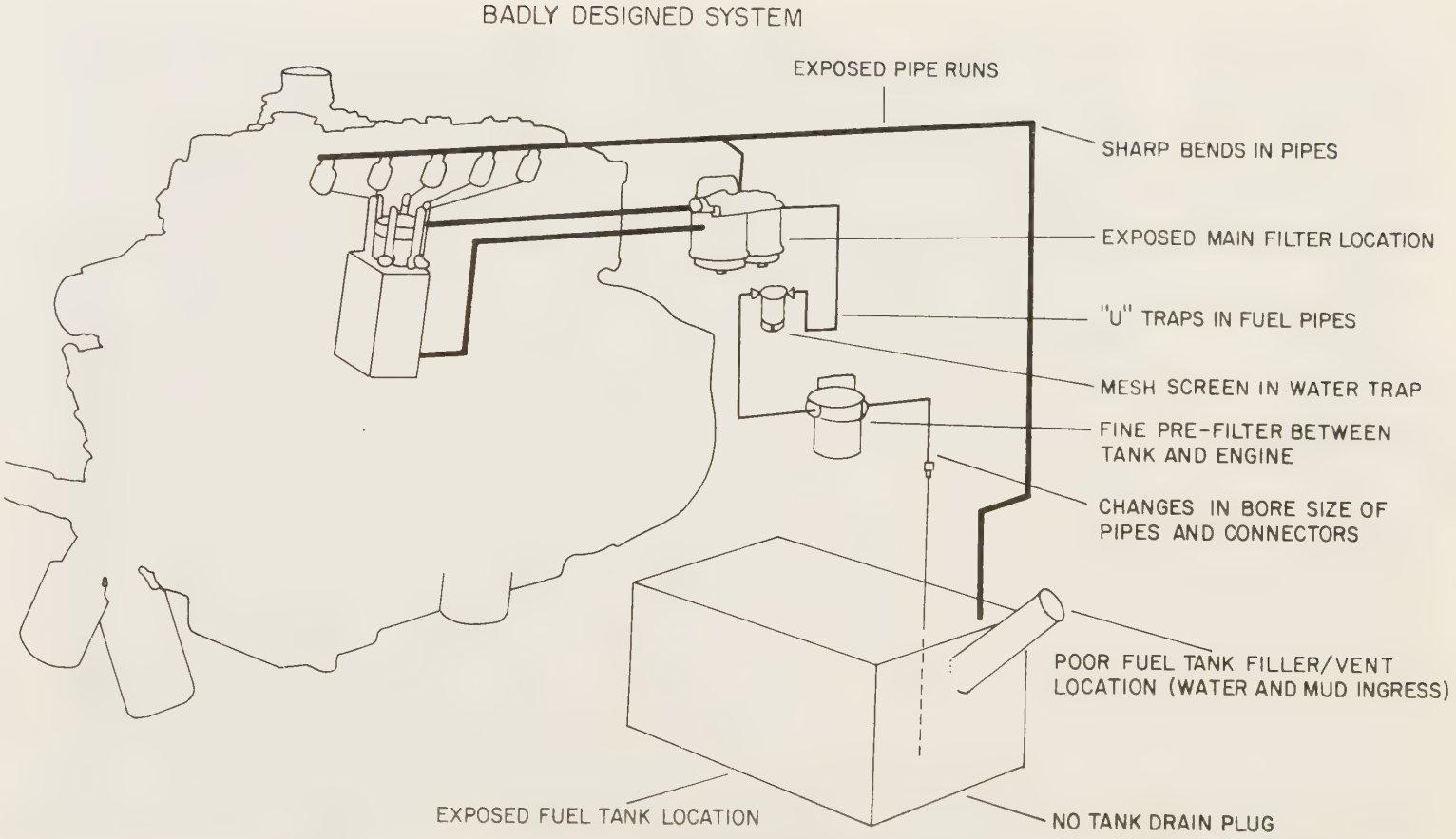
BADLY DESIGNED SYSTEM
EXPOSED PIPE RUNS
SHARP BENDS IN PIPES
EXPOSED MAIN FILTER LOCATION
"U" TRAPS IN FUEL PIPES
MESH SCREEN IN WATER TRAP
FINE PRE-FILTER BETWEEN TANK AND ENGINE
CHANGES IN BORE SIZE OF PIPES AND CONNECTORS
POOR FUEL TANK FILLER/VENT LOCATION (WATER AND MUD INGRESS)
EXPOSED FUEL TANK LOCATION
NO TANK DRAIN PLUG

FIG. 2. A badly designed fuel system.

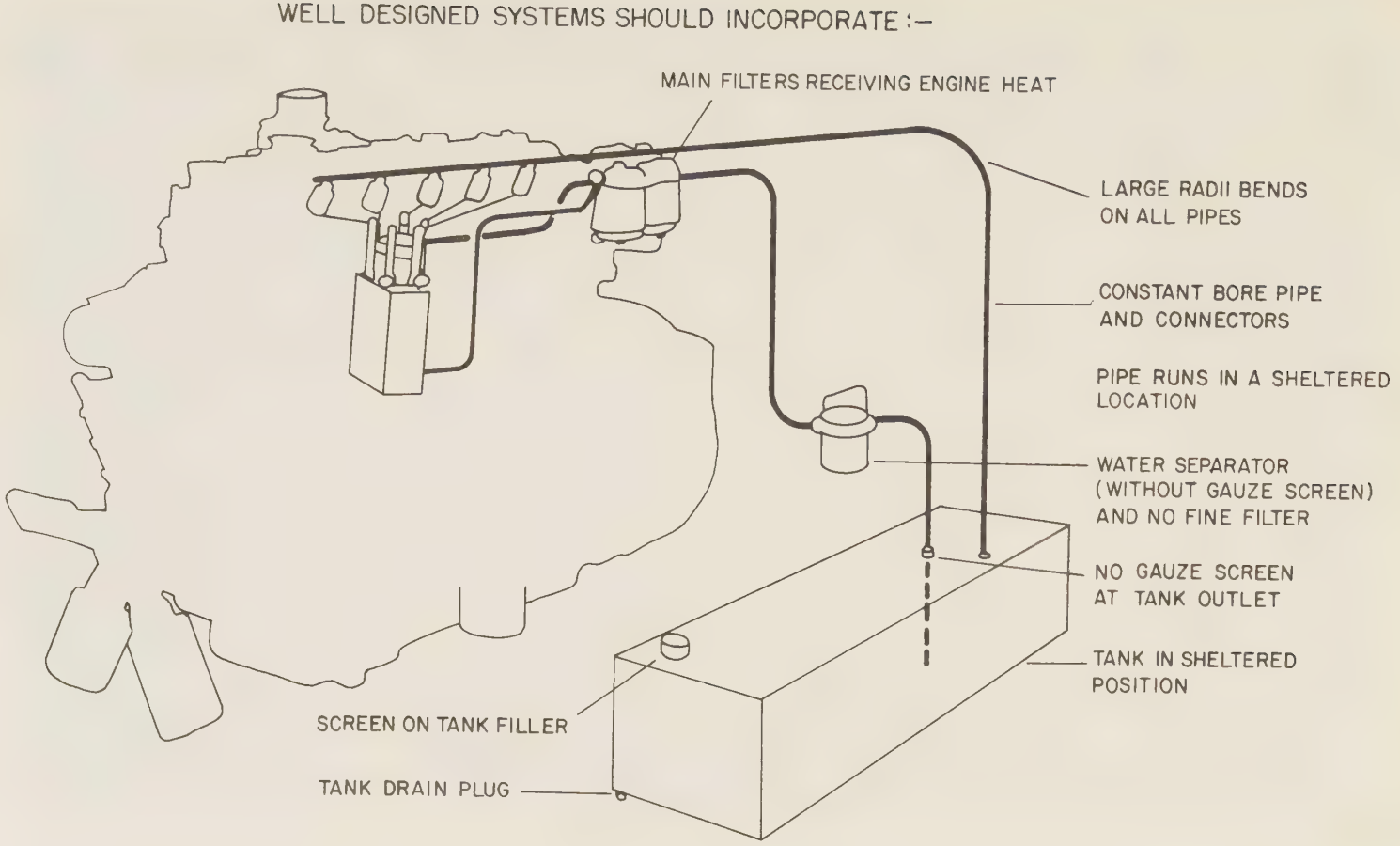
WELL DESIGNED SYSTEMS SHOULD INCORPORATE :–
MAIN FILTERS RECEIVING ENGINE HEAT
LARGE RADII BENDS ON ALL PIPES
CONSTANT BORE PIPE AND CONNECTORS
PIPE RUNS IN A SHELTERED LOCATION
WATER SEPARATOR (WITHOUT GAUZE SCREEN) AND NO FINE FILTER
NO GAUZE SCREEN AT TANK OUTLET
TANK IN SHELTERED POSITION
SCREEN ON TANK FILLER
TANK DRAIN PLUG

Fig. 3. A well designed fuel system.

illustrate good and bad fuel system design. This publication also contains other useful information on the low temperature problems that can occur with automotive vehicles and describes how to prevent them.

The Influence of New Refining Trends and Methods

The future availability of conventional petroleum fuels is threatened by exhaustion of known sources, the decreasing rate of new discoveries and limitation of supplies by political events so that governments at both national and international level have urged industry to consider ways and means of utilizing alternative energy sources.

Because petroleum most readily lends itself to the production of transport fuels, efforts have concentrated on developing alternative basic energy for electric power production and heating so that more of the crude oil can be converted into distillates suitable as transport fuels. The cracking processes necessarily involved in increasing distillate yields transfer more sulphur into the distillate stocks. With the advent of legislation to limit sulphur in distillate fuels such as gas oil used for diesel engines, there is the necessity to introduce hydrogen desulphurization. Hydrogen to effect this process may be obtained from the gasoline upgrading catalytic reforming process. By the cracking process sulphur is also concentrated into smaller quantities of the more viscous heavy residues which are marketed as marine fuel oils.

Gas oils produced from catalytic cracking are more waxy than those produced from straight crude distillation, and as a consequence means have had to be developed to mitigate the consequences of wax formation, or to invent dewaxing processes. As already mentioned additives have been developed and produced which will prevent the agglomeration of wax crystals in such a way that fuels remain fluid although the freezing point of the wax has been exceeded. Dewaxing of gas oils has not yet been economically justified in the UK, but the technology of hydrodewaxing of both fuels and lubricants using a zeolite shape selective catalyst has been fully explored and a fuel dewaxing plant is operating in Germany.[14] The process utilizes a simple inexpensive fixed-bed reactor similar in both capital and operating cost to an atmospheric gas oil desulphurization unit. The catalyst comprising an alumino-silicate crystal structure support carrying the active metals cracks selectively only the waxy crystals, leaving the other molecular structures unchanged. Since waxy paraffins have relatively low cracking rates over catalytic cracking catalyst, it is obviously beneficial to dewax cracking feedstocks rather than products, thus permitting the cracker to process additional charge.

Depending on product demand there may be several different ways in which catalytic cracking, hydrocracking, hydrodewaxing, and hydrodesulphurization might be integrated to produce different relative quantities of the traditional distillate range of fuels: gasoline, aviation kerosine, diesel fuel, and gas oil. Variations in quality may also be introduced. It is becoming increasingly important to have such flexibility to deal not only with changing patterns in demand, but also to cover the exigencies of political crises. There is a changing relative demand for diesel and petrol apparent in several European countries contingent upon the search for more economic transport. There are also changes in public reaction and legislation to the respective exhaust

emissions of the two types of engines which, together with fuel economy considerations, are leading to new engine designs. Some examples, such as spark-ignited diesel transgress the division between petrol and diesel engines so that fuels may likewise become unclassified. Alternatively, there will perhaps be a need for yet another category of engine fuel. Whatever situation may develop there is every reason to expect that catalysts such as the shape selective catalyst used for hydrodewaxing as well as for synthesizing distillates from hydrocarbon gases will play an increasingly important role in meeting specific quality requirements, or extending the yield of demanded fuels.

Alternative Diesel Fuels

It is true of most engines, but more specifically of diesels, that design can compensate for limitation in fuel features just as fuel features can compensate for design limitation. Recent concern about petroleum availability arising both from short term supply difficulties as well as the long term ultimate depletion of all petroleum oil, has stimulated the investigation of alternative fuels, although, in fact, the persistent ingenuity of scientists and engineers throughout many decades has explored adaptations to utilize many alternative fuels varying from gas, gasoline, and alcohols, to heavy residual oils, pulverized coal, and mixtures of coal and oil. Extension of fuel availability for the basic engines as known and understood has become increasingly important as dependence upon automotive power increases and the currently used fuels become vulnerable to threats of termination. Thus such fuels must be given preliminary attention in this chapter.

Whilst large diesel engines may be adapted to use crude oil or almost any fraction of it, smaller high speed engines must use distillate, and as demands are increased, production of residual fuel must diminish to meet these demands if excessive crude is not to be used. Extension of the yield of distillate is thus increased at the expense of residual product to meet the needs of road transport fuels. Any further extension of road diesel fuel availability must also look to the alternatives such as those available for extending gasoline, i.e., oxygenated fuels. Like the more volatile hydrocarbons the more readily manufactured methyl and ethyl alcohols are essentially bad diesel fuels on several counts:

(1) Poor lubricity.
(2) Low calorific value.
(3) Poor ignition quality.
(4) Corrosivity and low solubility in diesel fuel.

The adaptation for use in diesel engines has not been explored to any great extent for the good reason that the low calorific value of alcohols negates the big fuel economy advantage. Nevertheless when hydrocarbons are in limited supply diesel engines may be modified to use alcohols by introducing a dual fuel system, whereby injected conventional diesel fuel initiates the combustion and alcohol injected, or carburetted, provides the bulk of the total fuel input.

Another method tried has been to emulsify alcohol with conventional diesel fuel. This might be effected either by preparing and supplying stabilized emulsions at service stations, or dual fuel supply to a device on the engine which provides mechanical mixing of the two fuels before injection.

Some engine manufacturers, looking to the needs of less developed countries of the world, have examined a wider range of fuels originating from vegetable matter. Oils from seeds and nuts show greater promise for fulfilling the role of diesel fuels than as fuels for spark ignition engines. From tests which have been carried out many are shown to have acceptable cetane numbers, calorific value, and low or zero sulphur content. Viscosity, whilst high, can also be within acceptable range. Problems are mostly associated with gums and carbonaceous deposits in the fuel injection system, as well as high acidity causing some corrosion.

In the larger stationary engines fuels comprising pulverized coal, or slurries of pulverized coal in oil could be used, but would seem to pose excessive problems with respect to erosion of fuel system components by the particulate coal and erosion, corrosion, and deposit problems caused by the high ash levels of combustion products. Whilst theoretical predictions are often disproved by practical development and in this sense the prediction is made guardedly, it is considered that direct coal fuels will be used by indirect combustion engines such as the Stirling and steam engine. Even here the problems of the efficient heat exchangers which involve critical seals or intricate heat exchange surfaces are not easily solved with the type of fuels described.

The development of catalysis for producing hydrocarbon type fuels from coals and coal derivatives would appear to be a more fruitful approach to satisfying the needs of diesel engines, and most other types, than designing or adapting engines to use solid fuels.

The exploration of methods of producing fuels from various types of vegetation and biomass has gained momentum over recent years. Many such oils, which will be largely hydrocarbon in nature, can be usable as diesel fuels. The economics of manufacture and abundance relative to petroleum, or other mineral fuels, will probably be a more determining factor in their usefulness than the technical difficulties of adaptation they may present. However, in overcoming the technical difficulties, processing of the fuel, as suggested in the case of coal, may well prove a more viable proposition than adaptation of engine design.

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22

Domestic Fuels

By T. G. D. BARNETT and R. H. SHIPMAN

INTRODUCTION

The main petroleum fuels used for domestic heating fall broadly into two categories, the petroleum gases, i.e. LPG of which there are two, propane and butane, and the light oils, kerosine and gas oil.

Although gaseous at normal temperatures, petroleum gases can be liquefied by the application of comparatively low pressure, above atmospheric, and then stored in this state, becoming gaseous again when the pressure is reduced. Butane is the liquefied petroleum gas most commonly used for domestic heating appliances, particularly the so-called 'cabinet heater' where the butane cylinder is contained within the portable radiant flueless heater, and is also widely used as a source of heat and light for caravans and boats. Propane, either in cylinders or small bulk tanks which must be kept in the open air, is now becoming more popular as a fuel for both domestic installations and permanent caravan sites.

Kerosine, often referred to as 'paraffin', and gas oil are of course liquid at ordinary temperatures. They are distilled grades and therefore very low in impurities and non-combustibles, but are not so volatile as petrol. They are therefore easy to burn in proper appliances, but safe in storage tanks. Both have found wide application in domestic heating, from portable paraffin heaters, to full house central heating.

LIQUEFIED PETROLEUM GASES (LPG)

Specifications

All liquefied petroleum gases produced in the UK are manufactured within the quality specifications of BS 4250:1975. These are as follows:

Commercial propane specification. Commercial propane shall be a hydrocarbon mixture consisting predominantly of propane and/or propylene. It shall not contain harmful quantities of toxic or nauseating substances and shall be free from mechanically entrained water. It shall have the following composition and properties:

1. The total content of C_2 hydrocarbons shall not exceed 5.0 moles per cent, as determined by gas chromatography, mass spectrometry, or infra-red spectrometry.
2. The total content of ethylene shall not exceed 1.0 mole per cent, as determined by gas chromatography, mass spectrometry, or infra-red spectrometry.
3. The total content of C_4 and higher hydrocarbons shall not exceed 10 moles per cent, as determined by gas chromatography, mass spectrometry, or infra-red spectrometry.

4. The total content of C_5 and higher hydrocarbons shall not exceed 2 moles per cent, as determined by gas chromatography or mass spectrometry.
5. The vapour pressure at 45 °C (113 °F) shall not be greater than 17.6 bar (255 lbf/in² gauge), when determined by the method described in BS 3324.
6. The total content of sulphur (after stenching) shall not exceed 0.02 per cent by weight, as determined by the turbidimetric procedure described in the Institute of Petroleum method IP 243.
7. The content of mercaptan (after stenching) shall not exceed 0.005 per cent (m/m), as determined by method A described in BS 4386.
8. The hydrogen sulphide content shall not be greater than 0.5 ppm (v/v) (0.75 mg/m³ of gas volume), when determined by the method described in Appendix A of BS 4250.
9. The total content of acetylenes shall not exceed 2 moles per cent, as determined by gas chromatography or mass spectrometry.
10. The odour of the gas shall be distinctive, unpleasant, and non-persistent, and shall indicate the presence of gas down to concentrations in air of one-fifth of the lower limit of flammability. The lower limit of flammability for commercial propane may be taken as 2.4 per cent by volume in air.

Commercial butane specification. Commercial butane shall be a hydrocarbon mixture consisting predominantly of butane and/or butylenes. It shall not contain harmful quantities of toxic or nauseating substances, and shall be free from mechanically entrained water. It shall have the following composition and properties:

1. Ninety-five per cent by volume of the material shall evaporate at a temperature of 2.2 °C (36 °F) or lower, corrected to a barometric pressure of 760 mm Hg (29.92 in Hg).
2. The vapour pressure at 45 °C (113 °F) shall not be greater than 5.86 bar (85 lbf/in² gauge), when determined by the method described in BS 3324. Additionally, for the portable container trade only, the vapour pressure at 45 °C (113 °F) shall be not less than 4.85 bar (70 lbf/in² gauge), when determined by the method described in BS 3324.
3. The total content of dienes shall not exceed 10 moles per cent, as determined by gas chromatography or mass spectrometry.
4. The total content of sulphur (after stenching) shall not exceed 0.02 per cent by weight, as determined by the turbidimetric procedure described in the Institute of Petroleum method IP 243.
5. The content of mercaptan sulphur (after stenching) shall not exceed 0.004 per cent (m/m), as determined by method A described in BS 4386.
6. The hydrogen sulphide content shall not be greater than 0.5 ppm (v/v) (0.75 mg/m³ of gas volume), when determined by the method described in Appendix A of BS 4250.
7. The total content of acetylenes shall not exceed 2 moles per cent, as determined by gas chromatography or mass spectrometry.

8. The odour of the gas shall be distinctive, unpleasant, and non-persistent, and shall indicate the presence of gas down to concentrations in air of one-fifth of the lower limit of flammability. The lower limit of flammability for commercial butane may be taken as 1.9 per cent by volume in air.

Typical Properties and Physical Characteristics of LPG

Typical properties of LPG are shown in Table I. The significance of some of these properties, particularly in so far as they affect the applications of these gases, requires some elaboration. Liquefied petroleum gases are characterized by their high calorific values and a high degree of purity.

Vapour pressure. This is one of the most important characteristics of liquefied

TABLE I
Properties of Commercial Propane and Butane

	Propane	Butane
Relative density of liquid at 15°C (60°F)	0.50 to 0.51	0.57 to 0.58
Imperial gallons/ton at 60°F	439 to 448	385 to 393
Litre/tonne at 15°C	1 965 to 2 019	1 723 to 1 760
Relative density of gas compared with air at 15°C (60°F) and 1016 mbar (30 in Hg)	1.40 to 1.55	1.90 to 2.10
Volume of gas (ft^3) per lb of liquid at 60°C and 30 in Hg	8.6 to 8.7	6.5 to 6.9
Volume of gas (litres) per kg of liquid at 15°C and 1016 mbar	537 to 543	406 to 431
Ratio of gas volume to liquid volume at 15°C (60°F) and 1016 mbar (30 in Hg)	274	233
Boiling point at atmospheric pressure		
°C (approx.)	−45	−2
°F (approx.)	−49	28
Latent heat of vaporization (Btu/lb) at 60°F	154	160
Latent heat of vaporization (kJ/kg) at 15°C	358	372
Specific heat of liquid at 60°F (Btu/lb°F)	0.60	0.57
Specific heat of liquid at 15°C (kJ/kg°C)	2.512	2.386
Sulphur content, % weight	Negligible to 0.02	Negligible to 0.02
Limits of flammability (percentage of volume of gas in a gas–air mixture to form a combustible mixture)	Upper 10.0 Lower 2.4	Upper 9.0 Lower 1.9
Calorific values		
Gross (Btu/sft^3 dry)	2 500	3 270
(MJ/sm^3 dry)	93.1	121.8
(Btu/lb)	21 500	21 200
(MJ/kg)	50.0	49.3
Net (Btu/sft^3 dry)	2 310	3 030
(MJ/sm^3 dry)	86.1	112.9
(Btu/lb)	19 900	19 700
(MJ/kg)	46.3	45.8
Therm/ton (gross CV)	482	475
GJ/tonne	50.0	49.3
Air required for combustion		
(ft^3 to burn 1 ft^3 of gas at STP)	24	30
(m^3 to burn 1 m^3 of gas at STP)	24	30

petroleum gas, since it determines the pressure that will be exerted by the gas at ambient temperature, and therefore affects the requirements for handling and the designed working pressures of storage vessels. It constitutes the main difference in physical characteristics between commercial propane and butane. The vapour pressure is the pressure at which a liquid and its vapour are in equilibrium at any given temperature. The boiling point of a liquid is, in fact, the temperature at which the vapour pressure is equal to the external pressure.

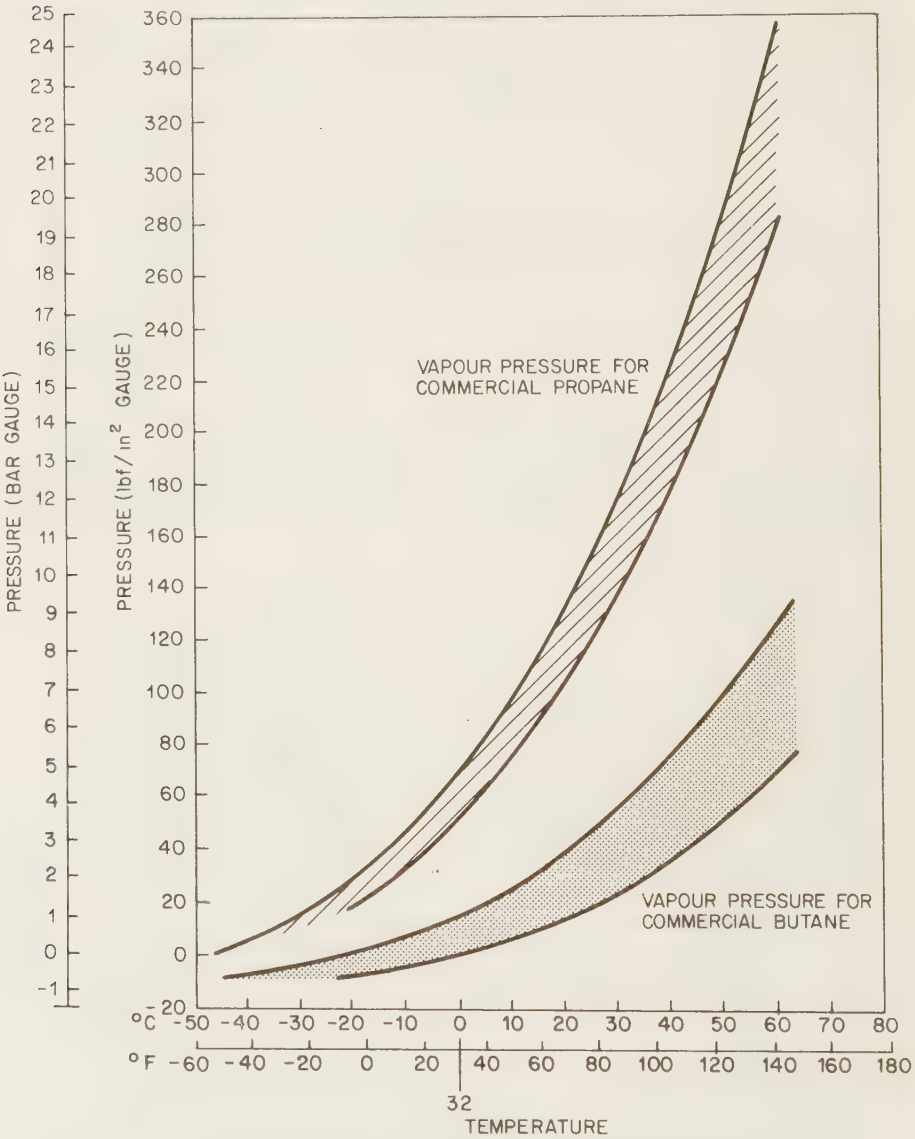

FIG. 1. Vapour pressure/temperature curves for commercial propane and commercial butane.

Commercial propane and butane often contain substantial proportions of the corresponding unsaturated analogues and smaller amounts of near-related hydrocarbons, as well as these hydrocarbons themselves. Figure 1 shows vapour pressure/temperature curves for commercial propane and commercial butane. Owing to its lower boiling point, higher rates of vaporization for substantial periods are obtainable from propane than from butane, and at the same time appreciable pressures are maintained even at low ambient temperatures.

Gross calorific value. This is defined as the amount of heat liberated when unit volume (or unit mass) of the gas is burned at a standard temperature and pressure. It is usually expressed in terms of Megajoules per cubic metre at 15 °C and 1016 mbar, i.e. MJ/sm³ dry or Megajoules per kilogram. Typical calorific values of LPG and other gaseous fuels are shown in Table II, and allow a comparison of their heating values to be made.

TABLE II
Typical Gross Calorific Values of Fuel Gases

Gas	MJ/sm³ dry	Btu/sft³ dry	MJ/kg	Btu/lb
Commercial propane	93.1	2 500	50.0	21 500
Commercial butane	121.8	3 270	49.3	21 200
Producer gas (cold)	4.7–6.1	125–165	—	—
Town gas	14–20.5	375–550	—	—
Natural gas	31.6–46.6	850–1 250	—	—
Acetylene	56	1 500	49.9	21 460

The great advantage of LPGs is that they are stored as a liquid; however, they are almost always used as a gas. One volume of liquid propane when released at STP gives 274 volumes (233 for butane) of high calorific value fuel gas.

Sulphur content. Compared to most other widely available fuels, with the exception of natural gas, LPG has a very low sulphur content which is strictly controlled within tight specification limits. This makes LPG a particularly useful fuel where the products of combustion are intended to be released direct into living accommodation.

Relative density—liquid. The density of liquid butane and propane is about half that of water, and as such is much lower than other liquid fuels.

Relative density—vapour. This is the one major property where there is an important difference between LPG vapour and natural gas. Natural gas is lighter than air; propane and butane vapour are, respectively, $1\frac{1}{2}$ times and twice as heavy as air. This is of importance in two areas. First, when converting equipment running on natural gas to run on propane or butane—the amount of gas which issues from a fixed orifice at a fixed pressure is inversely proportional to the square root of its density. Secondly, if there is a leak of LPG vapour it will collect at ground level or in depressions, drains or cellars, if appropriate precautions are not taken. This is a major safety consideration when designing or installing LPG systems.

Limits of flammability. LPG can only be ignited when mixed with air in certain proportions which lie between the limits of flammability. As a combustible gas

is gradually mixed with air in increasing proportions, a concentration is reached at which the mixture just becomes flammable. This is known as the lower limit of flammability. As the concentration of the gas in air is further increased, a point is reached at which the mixture ceases to burn, and the concentration of the gas just before this point is reached is called the upper limit of flammability. A flame can only be propagated in a gas/air mixture if the gaseous concentration lies within these points.

The limits of flammability for propane and butane are much narrower than most other gaseous fuels, making LPG much safer in this respect.

Coefficient of expansion. This is defined as the increase in volume of unit volume of a substance when its temperature is raised by one degree. It is important in that the coefficient of expansion of LPG in its liquid form is relatively high, so that when filling a storage vessel adequate space must always be provided to allow for expansion of the liquid.

Other physical characteristics. LPG is both colourless and odourless; however, a distinctive odour is added to aid detection in the case of leakage. BS 4250 requires sufficient stench to be added so that the odour of the gas can be detected in air at concentrations down to one-fifth of the lower limit of flammability, i.e. about 0.4 per cent gas in air.

Neither propane nor butane is toxic, but they do possess anaesthetic properties. There is a threshold limiting value for butane at 600 ppm, but there is no corresponding value for propane, the limiting factor being the reduction of oxygen content in the atmosphere.

Liquid propane and butane will vaporize rapidly if released into the open air, and if they come in contact with bare skin will cause painful freeze burns. Therefore gloves and goggles should always be worn if there is a danger of liquid LPG being released or spilt.

Storage and Handling of LPG

Butane. For domestic applications butane is stored as a liquid in portable cylinders. Cylinders are available in various sizes to suit applications with different rates of consumption. The most commonly available sizes contain 15 kg, 13 kg, and 7 kg of product.

Cylinders are, in the main, made from steel, although some are now being produced in aluminium, and are designed and manufactured to British Standard 5045 Part 2 (Part 5 for aluminium cylinders). Figure 2 shows a typical range of LPG cylinders, both butane and propane.

The valve outlet connection on butane cylinders used to have a male left-hand thread, but this is comparatively rare nowadays. Most butane cylinders now have a clip-on or snap-on type connection which enables the appliance regulator to be safely attached to the cylinder without the need for tools. However, there are a number of different designs of clip-on type valves in common use within the UK, and consumers should ensure that regulator and valve are compatible.

Butane is also found in disposable cartridges (see Fig. 3)—i.e. containers that are designed to be disposed of and not refilled when empty. Connection to these cartridges is by either a screwed valve connection which reseals when the appliance is removed, or is by piercing the cartridge at a specific point by the

FIG. 2. Range of steel LPG cylinders.

appliance. In the latter case the appliance may then only be safely removed when the gas in the cartridge is exhausted.

Codes of practice permit the keeping of butane cylinders inside domestic premises when they are attached to appliances. Spare cylinders must be kept outdoors in a safe place away from drains, cellars, and sources of heat. Similarly cartridges should be kept in a cool dry place, away from direct sunlight when not in use.

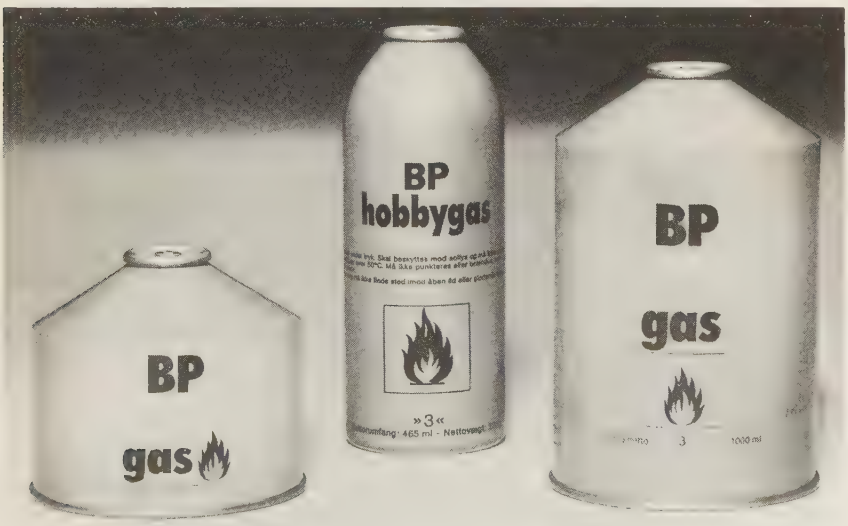

FIG. 3. Types of LPG disposable cartridges.

Propane is more commonly used for domestic applications when the equipment associated is of the fixed and permanently installed variety and connected to the propane storage by permanent rigid pipework.

The propane is stored as a liquid in either portable steel cylinders or in larger bulk static vessels. The cylinders, like butane, are designed and manufactured to BS 5045 Part 2, and need to be returned to a properly designed filling plant when empty for refilling. In practice the cylinder will be exchanged for a full one by a dealer representing the gas company, and it is the dealer who arranges the return of the cylinder for filling. Propane cylinders are available in many different sizes, but the 47-kg size is most commonly found for domestic applications; often two cylinders will be manifolded together, with an automatic change-over device to ensure continuity of supply. Propane cylinders are always placed outside (see Fig. 4).

Where the use of gas is high it is becoming increasingly common for a small static storage vessel to be installed (see Fig. 5). The vessel is permanently installed in a safe place and is refilled as required by a road delivery vehicle. The vessel will be designed and manufactured in accordance with BS 5500, and

Fig. 4. Two large propane cylinders manifolded.

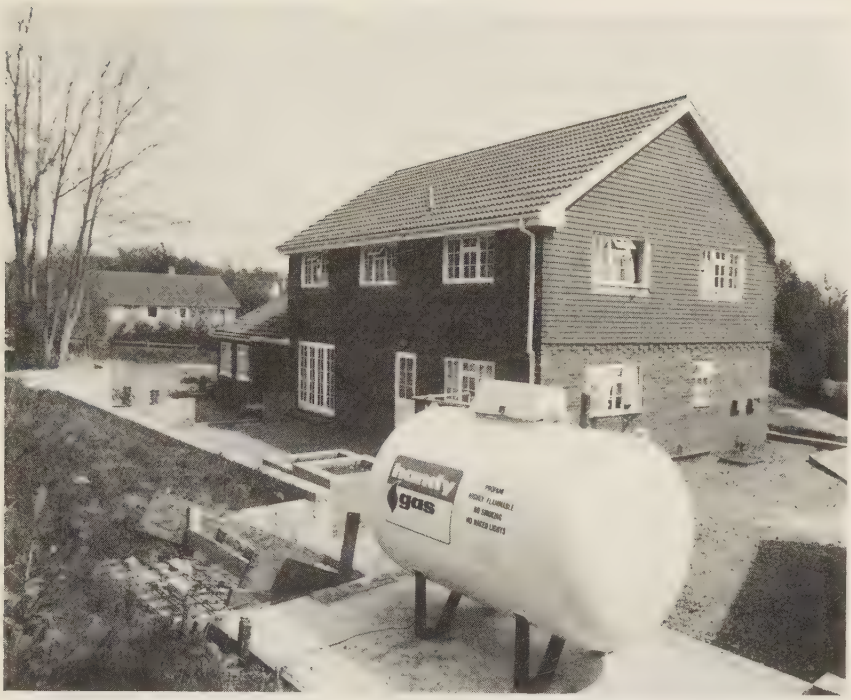

FIG. 5. Domestic installation of a small bulk LPG storage vessel.

will have a number of safety devices, including a relief valve designed to protect the vessel in the event of fire.

The valve outlet from both cylinder and vessel will have a right-hand female POL European connection, and this will require the appropriately sized spanner to ensure a leak-tight connection.

Applications of LPG for Domestic Heating

For many years the most commonly found domestic uses for LPG were mainly restricted to the leisure sector where they were used as a source of heat and light in caravans, tents, and boats. However, the discovery of natural gas in the southern North Sea led to large quantities of butane, which had been previously used for the manufacture of town gas, being made available. Subsequently, the discovery of the LPG-rich oilfields in the North Sea has led to an ever-increasing awareness of the possibilities of LPG for use as a domestic fuel.

LPG, because of its considerable similarity to natural gas, they are all members of the same homologous series of paraffin hydrocarbons, can be applied to virtually any item of equipment suitable for natural gas with only the change of injector jets. Indeed, most manufacturers producing natural gas equipment also offer a version to run on LPG. However, because LPG is easily liquefiable and can be kept in movable cylinders, there are some items of equipment which

have been designed to take advantage of this portability. This, therefore, means that domestic LPG appliances are not only found in areas where natural gas is not available, but also where gas is installed in a house yet there is still a need for a portable gas appliance.

Domestic LPG Appliances

The major growth in domestic LPG appliances has been in the area of the portable unflued radiant heater, commonly known as the cabinet heater. These heaters, as well as carving out a new market, have a very large section of what was traditionally catered for by the paraffin heater.

These heaters are designed to BS 5258 Part 10—'Safety of domestic gas

FIG. 6. LPG cabinet heater.

appliances—Flueless space heaters (excluding catalytic combustion heaters) (3rd family gases)', and have a maximum rated heat output of 4.75 kW (16 200 Btu/h). Their great attraction is that of being a stylishly designed gas-fired radiant heater that is also mobile. The mobility is achieved by including the cylinder containing the LPG within the heater itself. Though there are a variety of sizes of cylinder available for cabinet heaters, the most common contain between 13 and 15 kg of butane n.b. Propane cylinders are not used for this style of heater (see Fig. 6).

The great worry when these heaters were introduced was, as it is with any unflued appliance, that of vitiation of the atmosphere in the room where the heater is being used. Therefore one of the requirements of the British Standard is for an atmosphere sensing device. The device is required to shut off the main gas supply to the burners, when the appliance is in the hot condition, when the CO_2 content of the atmosphere lies between 0.8 per cent and 1.5 per cent. There are a number of different types, but nearly all consist of a pilot flame and a flame failure device. The key to this device is the state of the pilot flame. If the speed of the air–gas mixture and the flame velocity of that mixture are the same obviously the flame is stable. However, when the flame speed falls below that of the air–gas mixture then flame lift-up occurs. Now when the CO_2 content of the combustion air (i.e. room atmosphere) rises to about 0.8 per cent the flame speed is sufficiently altered (the air gas mixture speed is a function of the physical design of the pilot and the supply pressure and remains constant) for the flame to lift from the pilot. If the thermocouple of the flame-failure device is suitably placed this will cool when the flame lifts and shut down the gas supply to the heater.

Obviously the design of this device is that it will fail safe, i.e. if the pilot blows out gas flow is stopped, and also, having stopped the heater, it will not allow

Fig. 7. Range of LPG equipment to be run off cartridges.

relighting until the room atmosphere is corrected. The British Standard requires that 'any flame failure device shall open fully from cold in not more than 90 seconds and shall close from the fully heated condition within 90 seconds. Furthermore no device shall require more than 20 seconds of sustained manual operation before opening.'

The other area where LPG has been found more widely in the home is in the field of emergency equipment, i.e. portable stoves, lights and heaters, to be used in the event of a power cut. These items of equipment have been available for many years and widely used by campers and caravanners. These pieces of equipment run off the full pressure available from the butane; no regulating device is used as is the case with the cabinet heater (see Fig. 7).

OIL FUELS

Specifications

Oil fuels in the UK are generally controlled to the specification set out in British Standard 2869—'Petroleum Fuels for Oil Engines and Burners'. As its title suggests it covers a wide range of oil fuels, and for ease of reference each fuel is classified by a letter ranging from A to H. Fuels for burners range from C to H, covering from kerosine to heavy fuel oil.

Table III shows the specifications for fuels used for domestic heating; the classifications are as follows:

C1 Premium grade kerosine. A high-grade distillate intended for use in unflued heating appliances (paraffin heaters).

C2 Standard grade kerosine. A distillate grade used extensively for flued domestic heaters having vaporizing burners, and also for pressure-jet atomizing burners.

D Gas oil. A heavier grade distillate used for the larger domestic heaters with pressure-jet type atomizing burners.

The British Standard covers the basic requirements of each type of fuel for control purposes, placing limits on each property, and specifying the method of test to be used in its determination. There are other properties of the fuels which although not subject to control, are of interest for the user, and the designer of domestic heating equipment. Typical properties are shown in Table IV. For an understanding of some of these properties the following brief explanations are given.

Specific gravity

Both kerosine and gas oil are light hydrocarbons with an SG well below 1.00, and therefore lighter than water. Any water in storage tanks will therefore always sink to the bottom where the drain for its removal should be located.

Flash point

This is the temperature to which an oil must be heated, under specified conditions, to produce sufficient vapour to yield a flammable mixture with air.

TABLE III

Specificiations for Classes C and D Oil Fuels to British Standard 2869

		Class C1	Class C2	Class D	Test method
Viscosity, kinematic at 40°C	min	—	1.0	1.5	IP 71
	max	—	2.0	5.5	
Carbon residue—Ramsbottom % by mass on 10% residue	max	—	—	0.2	IP 14
Distillation					
Recovery at 200°C, % by volume	min	15	15		IP 123
	max	60	—		
Recovery at 357°C, % by volume	min	—	—	90	
Final boiling point	max	280°C	300°C	—	
Flash point—closed, Abel	min	43°C	38°C	—	IP 170
Flash point—closed, Pensky–Martens	min	—	—	55	IP 34
Water content, % vol.	max	Free from visible water	Free from visible water	0.05	IP 74
Sediment, % by mass	max	Free from visible water	Free from visible water	0.01	IP 53
Ash, % mass	max	—	—	0.01	IP 4
Sulphur, % mass	max	0.04	0.20	0.50	IP 107
Copper corrosion test	max	1	1	1	IP 154
Cold filter plugging point: Summer	max	—	—	0°C	IP 309
Winter	max	—	—	−9°C	
Smoke point, mm	min	35	20	—	IP 57
Char value, mg/kg	max	10	20	—	IP 10

The BS 2869 specifies the test method to be used. As these methods are quite time-consuming, there are quicker methods for spot checks. Placing minimum values on the flash-point temperature ensures that in proper storage domestic fuels are safe.

Viscosity

This is a measure of the resistance of a liquid to flow. Low-viscosity oil might be referred to as a 'thin' oil, and conversely, a high-viscosity oil might be called

TABLE IV

Some Typical Properties of Commercial Grades of Domestic Oil Fuels

	Premium grade kerosine Class C1	Standard grade kerosine Class C2	Gas Oil Class D
Density, kg/litre at 15°C	0.78	0.78 to 0.80	0.84 to 0.86
Viscosity, kinematic at 40°C	1.1 to 1.4	1.1 to 1.4	3.0 to 4.0
Smoke point, mm	38	25 to 28	—
Flash point (closed) °C	50	45	66
Sulphur, % mass	0.02	0.15	0.3 to 0.5
Ash, % mass	—	—	0.009
Water, % vol	—	—	0.045
CFPP March to September inclusive	—	—	0
October to February inclusive	—	—	−9
Calorific value, gross MJ/Kg	46.7	46.5	45.4

'thick. Domestic oil fuels at normal temperatures are quite fluid, not so different from water, but unlike water, the viscosity of oil is considerably affected by its temperature. The lower the temperature the higher the viscosity, i.e. it gets thicker. For the most part this is of no consequence for domestic oil fuel users. See also 'low temperature properties' (p. 854).

Viscosity is generally nowadays expressed as centistokes (cSt), but there are a variety of other units. Until recently a popular measure of viscosity for oil fuels was Redwood seconds, and kerosine and gas oil were often referred to as 28 seconds or 35 seconds fuel, respectively. These terms are now largely abandoned. There is no simple way of converting from one viscosity unit to another by calculation. Conversion factors are, however, given in many reference books.

Calorific value

This is the quantity of heat released by unit quantity of fuel, when it is burned completely with oxygen, and the products of combustion returned to ambient temperature. This quantity of heat will include the heat of condensation (latent heat) of the water vapour formed by the combustion of the hydrogen in the fuel, as it cools to ambient conditions. It is called the 'gross calorific value' or 'higher calorific value'.

Most heating applications cannot recover the heat of the water vapour; it simply escapes with the vapour out of the chimney. The potential heat content is therefore more nearly indicated by subtracting this latent heat from the gross CV, and the resultant value is called the net calorific value, or lower calorific value.

The efficiency of domestic heating equipment is often quoted by manufacturers, being the percentage of the heat in the fuel released as useful heat into the room, or into the boiler, etc. It is very important to know whether the quoted efficiency is based on the gross, or the net, calorific value. The difference is significant. UK practice has been to use gross CV, but Continental and US practice has been to use net CV, which for exactly the same appliance will give a much higher efficiency figure.

The heating value of any fuel, or source of energy, is the amount of useful heat which can be extracted from it. Thus a knowledge of the calorific value of the fuel, and the efficiency of the heating equipment, is essential to compare the merits and running costs of different fuels and energy sources. Table V shows the gross calorific values, the thermal equivalents and typical utilization efficiencies of domestic fuels, and electricity.

Sulphur content

Sulphur is present in all fossil fuels. In the production of domestic oil fuels, however, steps are taken to ensure that the levels are kept within the very low levels specified by BS 2869. In the UK there is also a legal requirement to observe a maximum permitted sulphur level of 0.5 per cent by weight in gas oil used for heating purposes.

The sulphur in the fuel burns readily to sulphur dioxide and is released with the other products of combustion. For premium grade kerosine (Class C1)

TABLE V
Calorific Values and Utilization Efficiencies of Domestic Fuels

Fuel	Gross calorific value	Thermal equivalent	Utilization efficiency (approx.)
Oil (vaporizing)	158 000 Btu/gal	1.58 therms/gal	75%
Oil (atomizing)	165 000 Btu/gal	1.65 therms/gal	75%
Anthracite	14 000 Btu/lb	15.68 therms/cwt	70%
Coke	12 000 Btu/lb	13.44 therms/cwt	65%
Gas (town)	500 Btu/ft^3	1 therm/200 ft^3	75%
Gas (natural)	1 000 Btu/ft^3	1 therm/100 ft^3	75%
Electricity	3 412 Btu/kWh	1 therm/29.3 kWh	100%

which is used indoors in unflued appliances, the level of sulphur is therefore kept extremely low. The combustion of other oil fuels will release the SO_2 to atmosphere via the chimney.

Smoke point

A factor of some significance in the acceptability of oil-fired domestic appliances is the absence of visible smoke. Modern oil-burning appliances properly adjusted and operated make no visible smoke. The smoke point of the oil fuel is more critical, however, when it is to be burnt in the wick-type burners employed in flueless heaters. In this application the smoke point is a factor in limiting flame height and therefore the heat output of the appliance. The tendency of kerosines to smoke is mainly dependent on their hydrocarbon type. The greater percentage of elemental carbon in aromatics, compared with paraffinic hydrocarbons, means that high-aromatic fuels will smoke more readily, and hence aromatics may have to be removed during the manufacture of heating kerosines.

Char value

The amount and nature of the deposits (char) produced on a wick during combustion depend on the hydrocarbon composition of the fuel and also on the design of the appliances in which it is used. Char occurs as a result of the breakdown and decomposition of the kerosine under the local conditions existing at the wick surface, and these conditions will also determine what proportion of the decomposed products remains on the wick.

Carbon residue

The Conradson Carbon Residue test gives an indication of the amount of carbonaceous material formed by a gas oil when this is burned in a limited supply of air. Although originally designed for assessing the quality requirements of a diesel fuel, it finds a place in the domestic fuel specifications as an indicator to detect the presence of excessive amounts of higher-boiling materials which might cause excessive carbon formation in pressure-jet

burners. The burning tests for kerosine and the carbon residue test for gas oil are carried out under laboratory conditions, and it may therefore be suggested that they do not truly assess the burning performance of these fuels in the wide variety of equipment used in domestic heating. Such tests are, however, essential in maintaining the necessary standards of product quality, and many years' experience has shown that the fuels controlled by these tests give results in all types of appliance very much in line with what is expected.

Additives, dyes, and re-odourants

Some kerosines, particularly those sold for flueless appliances, are dyed a characteristic colour for purposes of sales promotion and identification. Domestic gas oil fuel for central heating must by law contain a red 'tax' dye. In addition, both undyed kerosines and domestic gas oils must contain statutory chemical markers in the appropriate amounts. The presence of these markers does not interfere with the burning qualities of the fuels, and is used only as a detector should it be suspected that the fuels are being used as road diesel fuels without payment of the higher rate of tax. Some premium grade kerosine may also contain additives to inhibit rusting of containers in free-standing appliances by traces of condensed water, and also to 'neutralize' the faint, but characteristic, odour of the product which some users find unpleasant.

Cold Filter Plugging Point (CFPP)

It is essential, so far as is reasonably practicable, that operating difficulties should not arise with domestic oil fuels during low-temperature conditions in winter. As its temperature is continuously reduced a distillate fuel will increase in viscosity, but more important, at a certain low temperature it will start to precipitate small wax crystals. On reheating these dissolve back into the fuel, and it is this temperature which is called the freezing point for kerosines in Table IV.

Cold weather is unlikely to give any problems for kerosine, but gas oil deserves further examination. Because oil fuels do not freeze in the same way as water, a test method had to be developed which would reflect as nearly as possible actual operating performance in a fuel system. Domestic oil fuel is usually kept in storage tanks in the open, and led by pipework, which is often exposed, into the house. The oil fuel, particularly that in the pipeline, will therefore respond to the ambient temperature. The test devised is called the cold filter plugging point (CFPP) and was incorporated in BS 2869 by an amendment in 1977. The test consists of drawing a measured quantity of fuel through a fine, mesh filter at successively lower temperatures. The CFPP temperature is that occurring when the fuel flow rate drops to a specified unacceptable level.

In setting the CFPP temperatures shown in Table III a considerable study of UK winter weather data was undertaken. Prolonged air temperatures below minus 9°C (15°F) are rare in the UK, and thus this value was used for the winter grade. BS 2869 permits gas oil to be sold during summer, i.e. from 1 March to 30 September, with a higher CFPP of 0°C (32°F). Thus summer-grade gas oil still in a fuel tank during cold winter weather might create

problems unless precautions are taken. Fuel suppliers will be very willing to provide further guidance on this.

Storage and Handling of Domestic Oil Fuels

Oil fuels for domestic heating have been in use for a long time, and there is now a great deal of experience on good practice for storage and handling. Much of this has been compiled into the following British Standards:

BS 799—Oil Burning Equipment
- Part 1—Withdrawn.
- Part 2—Vaporizing burners.
- Part 3—Automatic and semi-automatic atomizing burners up to 36 litres/h and associated equipment.
- Part 5—Oil storage tanks.
- Part 6—Safety times and safety, control, and monitoring devices for atomizing oil burners of the monobloc type.

BS 5410—Part 1—Oil Firing. Installations up to 44-kW output capacity for space heating and hot water supply purposes.
- Part 2—Oil Firing. Installations of 44-kW and above output capacity for space heating, hot water, and steam supply purposes.

The domestic consumer generally stores his fuel in a steel storage tank, usually out of doors and within a short distance of the boiler or other oil-fired appliance. For an average sized heating system of up to, say, 11.7 kW (40 000 Btu/h) a tank with a working capacity of 1000 litres (200 gallons) would be adequate. The steel tank (not galvanized) should be supported on brick or concrete piers, or a steel frame, and given a slight slope down towards the drain valve, which should be at the opposite end from the oil supply line to the heating appliance. The tank requires a fill connection pipe with a threaded end to take the delivery tanker hose coupling, and because the tank is totally enclosed it needs a vent at least the size of the fill pipe. If the vent is a pipe, it must be very short, and terminate at a height which will not over-pressurize the tank in the event of an over-fill. Other fittings required are a drain valve, an isolating valve in the line to the heating appliance, and a contents gauge. Full details are included in BS 799.

The oil supply to the appliance is usually by gravity, and the height of the tank must therefore be arranged to suit, and to meet the maximum and minimum head of oil above the burner specified by the burner manufacturer. The pipeline is usually annealed copper or mild steel (not galvanized). A filter is usually incorporate in the supply line, and where it enters the house a fire-valve is required. This is a valve held open by a fusible link. In the event of a fire, the fusible link melts, and the valve shuts, thereby avoiding the possibility of the fuel feeding the fire.

Unlike heavy fuel oils, domestic fuels do not require any heating in storage. However, attention has already been drawn to the effects of very cold temperatures on gas oil. The fuel specification allows for very cold conditions

rarely met in the UK but, however, there are the freak conditions which have given rise to arctic temperatures. It is therefore prudent to minimize the effects by avoiding the more exposed locations for tanks, and particularly pipelines. The lagging of exposed pipelines and fittings will reduce the risks still further.

Central Storage and Distribution Schemes

Where a housing estate, or a low-rise development is heated by individual oil-fired heating systems, the fuel may be distributed from a central storage scheme. One or more bulk fuel storage tanks are installed at a central point, and the oil is supplied to the consumers via a network of underground pipes, with branches to a fuel meter at each dwelling. These systems are often installed and operated by the fuel supplier, who services the storage and distribution system, arranges for the meters to be read, and invoices the consumers accordingly.

Combustion of Domestic Oil Fuels

Oil fuels do not burn in their liquid state. They have to be in the form of a vapour and mixed with the oxygen in the air in the correct ratio to form a combustible mixture.

All petroleum oils vaporise to some extent when exposed to the atmosphere, and the rate will markedly increase if the oil is heated. Gasoline evaporates rapidly at ordinary ambient temperatures, but kerosine evaporates more slowly, and gas oil even more slowly. To achieve satisfactory combustion of kerosine or gas oil used in domestic burners, it is necessary to increase the evaporation rate considerably. The means of achieving this rely on two factors: increasing the surface area of the oil to be burned, and increasing its temperature. The two types of burner design which achieve this fall into either vaporizers or atomizers.

Vaporizers rely on the inherent volatility of kerosine fuels being sufficient if supplementary heat is available. Once ignited the heat derives from the flame itself. The wick in a wick-type burner provides the motive power to keep its surface continuously supplied with fuel. Other types rely on a very shallow layer of kerosine being continuously heated by flame radiation to provide the vaporization.

Atomizing burners break up the fuel into a very fine spray which increases the surface area enormously and enables the heat from the flame to create the required vaporization. It also of course enables the oxygen in the air to mix rapidly with the droplets and vapour to secure clean combustion. This method of combustion is used for both kerosine and the gas oil.

The most efficient combustion would occur if the oil fuel could be brought into intimate contact with the oxygen in the air, in the chemically correct proportions of 1 part oil to 15 parts air. This is because any extra air supplied plays no part in the combustion and, like the nitrogen, simply adds to the amount of heat carried away in flue gases. But a burner supplied with just this quantity of air would emit black smoke and soot, because it is never possible to mix the air and oil sufficiently rapidly, and some oil never finds all the oxygen it requires and ends up as a carbon particle. To overcome this, excess air is used,

giving the oil more chance to find its oxygen. The burner designer strives to achieve smoke-free combustion with the minimum amount of excess air, since the lower the excess air the lower is the loss of heat up the chimney—the stack loss.

Modern oil burners will operate entirely smoke-free and with minimum maintenance, when set up correctly. Regular maintenance is desirable to ensure that the burner is set to optimum conditions. Poorly maintained burners may tend to emit smoke, and accumulations of soot on the heating surfaces will reduce efficiency. On the other hand, maladjustment which permits too much air to the burner may go unnoticed and yet will simply result in more fuel being used than is necessary because of excessive stack losses.

It can be stated as a general rule that if an oil burner is operating without creating smoke then virtually all of the oil is being burned completely to carbon dioxide and water vapour. By using suitable instruments the amount of CO_2, or even more directly the amount of oxygen in the flue gases, the amount of excess air can be determined. This needs to be kept to a minimum whilst ensuring smoke-free conditions to achieve the highest fuel efficiency. Manufacturers will provide a guide as to the CO_2 or O_2 readings which can be achieved.

Oil Burners

Portable flueless heaters. Burners for portable convector heaters, familiarly known as paraffin heaters, are usually of the annular wick type. The bottom of the wick lies in the fuel container and extends up through the wick carrier. The oil is raised to the top of the wick by capillary action. The oil is lit by hand and burns off the wick at a rate depending on the amount of wick exposed.

Burners for portable radiant heaters are of the short drum type. The burner is fed with oil from a container in the base of the heater, and the burning rate is controlled by a metering valve. An annular wire coil and a hemispherical grid on top of the burner glow red hot and provide some radiant heat which is reflected forward by a polished metal reflector.

Portable room heaters are unflued so the products of combustion, i.e. CO_2 and water vapour, are released into the room. This gives a very high efficiency, but the room must have adequate good ventilation. Also for this reason the highest quality kerosine (paraffin) should be used, i.e. Class C1. This will ensure complete combustion, minimum odour, and the minimum of sulphur dioxide.

Oil burners for flued appliances. There are two main types of oil burners used for domestic central heating boilers. These are vaporizing burners and pressure-jet burners. In the early days vaporizing burners using class C2 kerosine were the most common, because they were much quieter in operation, and were better able to operate at the low throughputs required by the average sized house. Recent developments in the design of domestic pressure-jet burners have, however, changed this situation. Pressure-jet burners are now available down to outputs of around 12 kW (41 000 Btu/h) using class C2 kerosine, and are considered quiet enough for installation in kitchens. Vaporizing burners are still quieter in operation, since there is virtually no combustion noise at all, and these are still available.

Vaporizing Burners

There have been a number of different, often ingenious, designs of vaporizing burner. One of the most commonly available designs is now the forced-draught pot burner (Fig. 8). These operate automatically in an on–off cycle as dictated by the boiler thermostat. The burner consists of a cylindrical metal pot with perforations around it through which combustion air is forced by a centrifugal fan. The ignition sequence starts with a purge period, followed by admission of fuel to the pot, and the energizing of an electric ignition heater coil. The igniter heats the fuel which starts to vaporize and ignites. The heat radiated from the combustion promotes further vaporization and the flame rises up the pot, finally stabilizing at the top as a typical pre-mixed blue flame combustion. The heat of the flame radiating downwards is then sufficient to vaporize the fuel at the rated input, and the electric igniter is then automatically switched off.

The burner operates continuously until the boiler thermostat reaches maximum setting, when it will initiate the shut-down sequence. This involves shutting the fuel feed valve, but leaving the combustion air fan on for several minutes to ensure complete purging before it also is switched off.

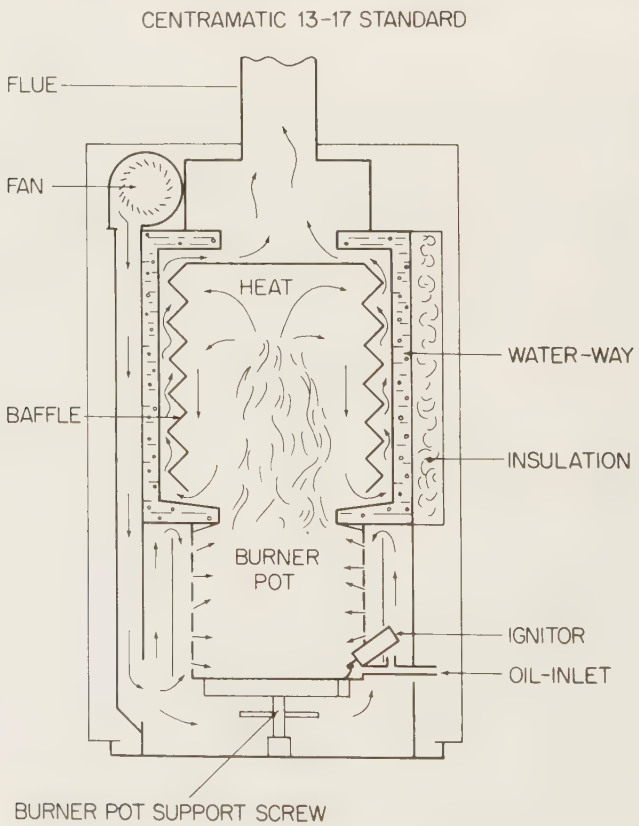

Fig. 8. A forced draught pot burner (Trianco-Redfyre Ltd).

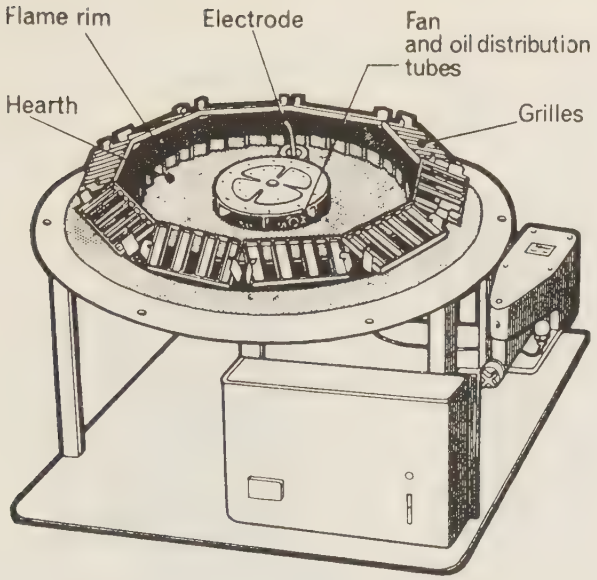

FIG. 9. A typical rotary vaporizing burner of the wallflame type.

The basic requirements for automatic safe light-up and shut-down, and flame-failure controls for vaporizing burners are contained in BS 799 Part 2.

Another type of vaporizing burner which is still in use includes the very popular rotary type, often referred to as the 'wallflame' burner.

The operation is best understood from the illustration Fig. 9. The principle is that the fuel is fed to a central rotor with radial oil distributor nozzles. When the rotor rotates oil is ejected radially as a fine spray so as to impinge on the circular hearth. The central rotor often incorporates the primary combustion air fan.

The burner operates automatically in an on off sequence as dictated by the boiler thermostat. The start sequence includes a purge period when the fan-rotor operates without fuel, and in some designs by heating of the hearth. High-tension electrode ignition is then switched on, followed by admission of the fuel which immediately ignites. The flames stabilize on the hearth and quickly heat up to promote rapid vaporization and a stable 'wall' of flame. The heat radiating from the wall of flame is then sufficient to vaporize the fuel at the rated input, and the igniter and heater are switched off.

The safe start-up, shut-down, and flame-failure controls for these burners are set out in BS 799 Part 2.

Atomizing Burners

The pressure-jet burner is now the most commonly available type of domestic burner and is fitted to a wide range of central heating boilers (Figs 10 and 11). They are available for boiler ratings of as low as 12 kW (41 000 Btu/h) and are offered for kitchen installation.

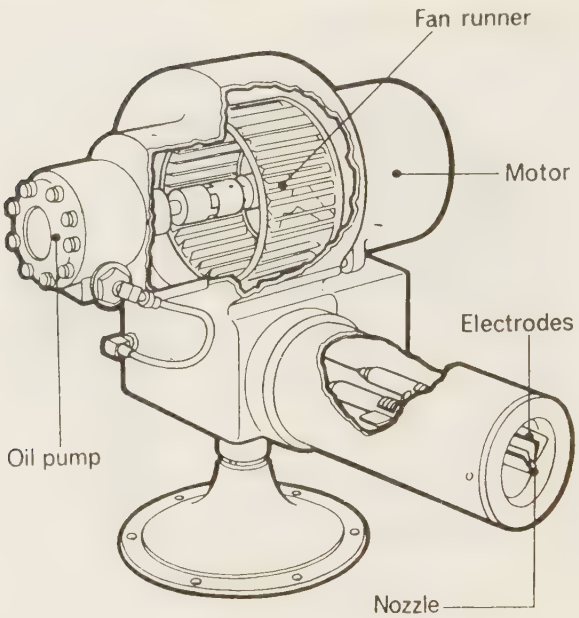

FIG. 10. A typical pressure-jet burner.

Pressure-jet burners are suitable for Class C2 kerosine, but above about 17 kW (5300 Btu/h) are often available to operate on the cheaper Class D gas oil.

The principle of a pressure jet is simply to force the fuel through a small orifice nozzle at high pressure, say 100 lb/in^2. The nozzle is a very carefully designed and engineered device which has a tiny swirl chamber immediately before the final orifice. This imparts extremely rapid rotation to the fuel, with the result that as it issues from the orifice, it resembles a hollow cone which immediately breaks up into a very fine spray and is easily ignited.

The burners are designed as compact units incorporating an electric motor driven fan and fuel pump, usually on a common shaft, with the nozzle and combustion air contained in a horizontal extension or blast-tube which projects into the boiler. It resembles the barrel of a gun, and is sometimes referred to as a 'gun type burner'. At the end of the blast tube the burner head consists of the nozzle, the flame-stabilizing device, and the ignition electrodes. All of these have to be very carefully positioned, based upon the manufacturers' recommendations, to ensure flame stability and good clean combustion. The air supply can be adjusted during commissioning by means of dampers or air slides, so that the excess air is reduced to a minimum consistent with clean combustion, and so to achieve very low stack losses. The latest designs are also much less sensitive to adverse flue conditions.

Domestic pressure-jet burners operate automatically on an on–off cycle at the call of the boiler thermostat. The ignition sequence is, as for other types of burner, preceded by a purge period when the fan operates but the fuel supply valve is shut. This is followed by the energizing of the spark electrodes of the

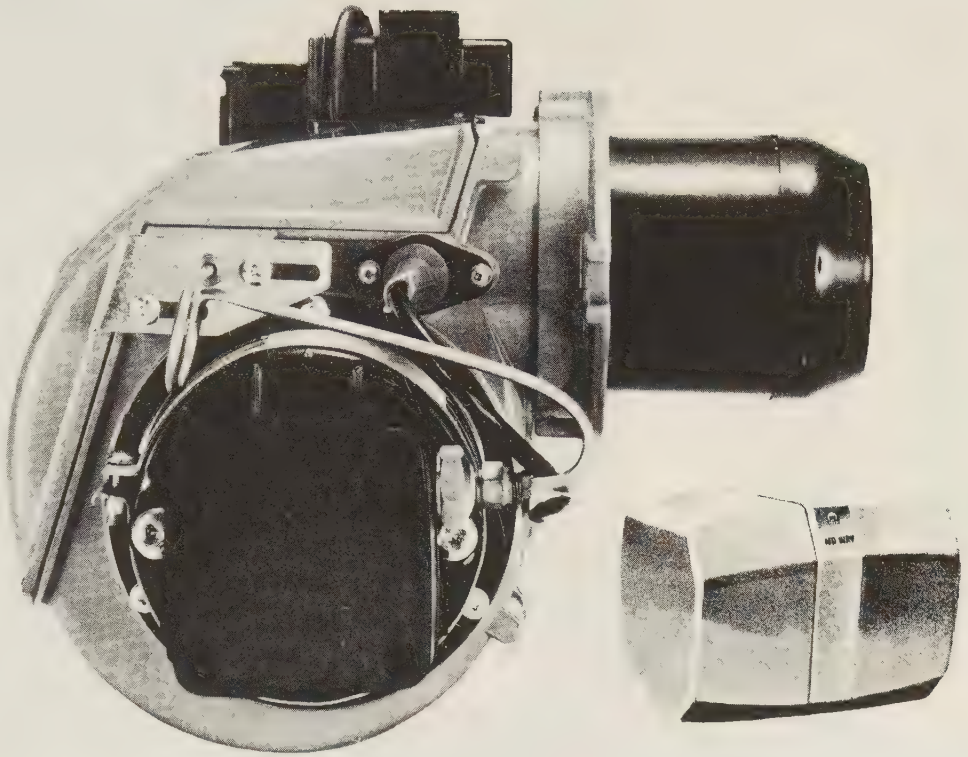

FIG. 11. A modern pressure-jet domestic burner (Nu-Way Heating Plants Ltd).

igniter and the opening of the fuel valve. Pressure-jet atomization is so fine that ignition is virtually instantaneous. Once the flame is established the igniter is usually automatically switched off. The combustion is then continuous until the boiler thermostat initiates the shut-down sequence. Again, the fan will continue to run after the fuel valve has closed to provide the post-purge period and ensure that no flammable products remain in the system.

The basic requirements for automatic safe light-up, shut-down, and flame-failure controls for pressure-jet burners are contained in BS 799 Part 6.

Domestic Oil Burning Appliances

Portable flueless space heaters. Reference has already been made to these appliances under 'Oil Burners' in describing their operation. Despite the competition from LPG cabinet heaters they still enjoy a demand for an inexpensive form of heat in the UK. Both radiant and convector types are available. Considerable work

FIG. 12. A free standing flueless convector heater (Valor-Veritas Ltd).

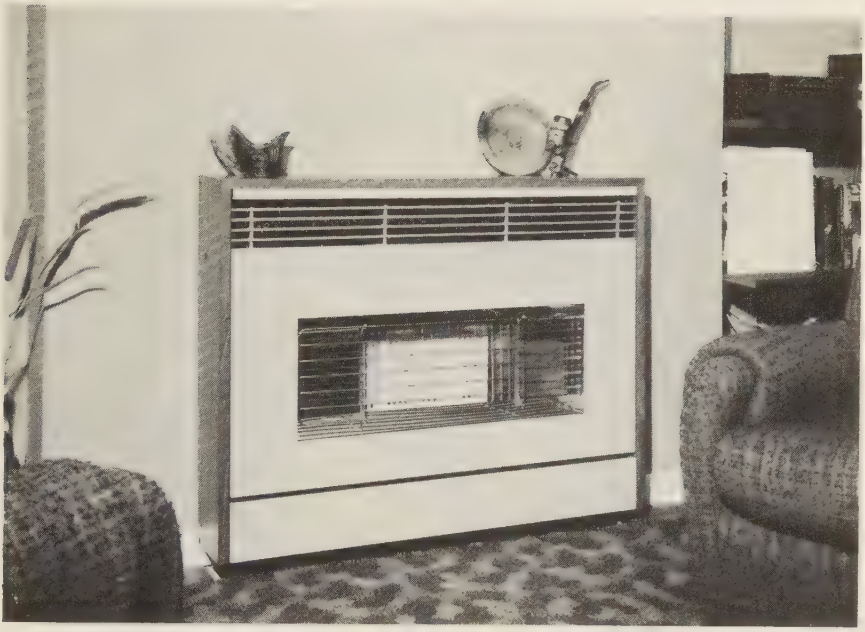

FIG. 13. A flued radiant heater (Taylor and Portway Ltd).

has been done to ensure the safety of these appliances, and in the UK they have by law to meet minimum design requirements set out in BS 3300—'Kerosine (Paraffin) Unflued Space Heaters, Cooking and Boiling Appliances for Domestic Use'. This sets out standards for the stability of a floor-standing heater, safety in overturning, emission limits of carbon monoxide, control of smoke emission, maximum allowable surface temperatures, etc.

Flued radiant heaters. These are fixed appliances providing radiant and convective heat in living rooms where a conventional flue and fireplace are available. They can incorporate a domestic hot-water system, and in some cases can run one or more radiators.

Domestic boilers. Oil-fired domestic hot water boilers employ either the vaporizing burner or the pressure-jet burner. The trend over recent years is towards pressure-jet burners, even for quite small boilers around 12 kW (41 000 Btu/h) as described earlier. Noise levels have been reduced and are regarded as quite acceptable for kitchen installation. Physical dimensions are smaller and there are wall-mounted versions available. A typical kitchen-installed boiler is shown in Fig. 14.

Another trend worthy of mention is the use of the low-level discharge flue. Hearths and flues of domestic boilers have to comply with the Building Regulations. Normally this requires a flue and chimney terminating above the roof. In some cases it is more convenient to use a low-level discharge, installed directly through an external wall with a suitable flue terminal and guard. It is usual for such installations to follow the *Guide to Good Practice* issued jointly by the HVCA and the IHVE. There is rarely any difficulty in obtaining the

FIG. 14. A kitchen installed domestic boiler (Trianco-Redfyre Ltd).

approval of the local building inspector to such an installation. A simple illustration of the arrangement is illustrated by Fig. 15.

Occasionally, due to local conditions, there is a call for reducing the noise from low-level flues. A low-level flue terminal silencer is illustrated in Fig. 15.

Domestic air heaters. An alternative to hot water central heating is the warm air system. There are many installations in service, and various designs are available from flued convector units, some with radiant panels, to brick central units built in to the house structure. Most of these are available with a domestic hot water facility. A typical kitchen installed unit is shown in Fig. 16.

Brick central units are usually designed to operate on natural convection. Cool air is admitted through grilles at low level in the brick or concrete heater chamber and warmed as it passes over the heat exchanger and then discharged at high-level grilles serving adjacent ground-floor rooms. Heat convected upstairs through the stair well provides a comfortable temperature in the bedrooms. Some designs use fan assistance to distribute the warm air.

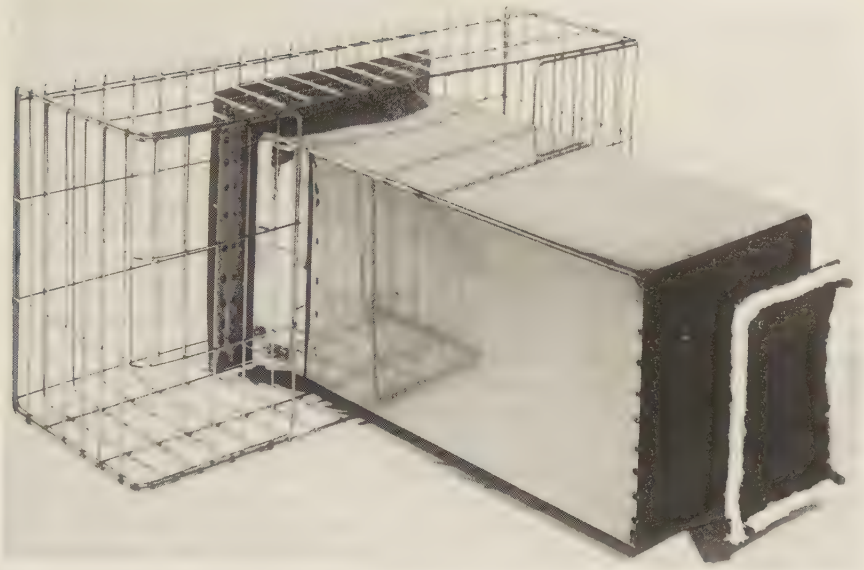

FIG. 15. A low-level flue silencer (Trianco-Redfyre Ltd).

FIG. 16. A domestic warm air heater (AFOS Ltd).

Ducted warm air units either use a direct-fired heat exchanger, or an indirect system where a boiler circulates hot water through a water–air heater exchanger. The warm air is distributed throughout the house by a fan and ducted system.

Warm air systems are generally only suitable for new houses where the heating system is an integral part of the design.

In the UK there is an independent testing and approval service known as DOBETA. This was formerly the Domestic Oil Burning Equipment Testing Association, it is now simply DOBETA, and it has extended its facilities to commercial and industrial equipment. It is a non-profit making organization with a Council of Management with representatives from the Oil Companies, British Standards Institution, the Building Research Establishment, the Fire Research Station, and Warren Spring Laboratories.

As far as domestic appliances are concerned DOBETA undertakes the testing of oil-fired appliances together with their ancillary components and fittings and also water thermostats, oil control valves, automatic burner controls, and fuel pumps. They have devised and maintain standards of test which have now been adopted and published as BS 4876. An appliance undergoes a series of comprehensive and searching tests and inspection procedures to assess its safety and reliability in operation, followed by performance testing during continuous running under simulated service conditions.

Provided an appliance meets the relevant specification criteria and the producing factory satisfies pre-licence inspection the manufacturer is granted a Certificate of Approval in respect of that particular model which is valid for five years, and allows the manufacturer to use the DOBETA Approved symbol on production models.

A quarterly list of tested and approved domestic oil burning appliances is distributed free of charge to local authorities, fuel distributors, heating installers, equipment manufacturers and others concerned with selling oil fired heating.

List of British Standards

BS 4250 Commercial butane and propane.
BS 4386 Method of determination of mercaptan sulphur content in light hydrocarbon products.
BS 3324 Method of determination of vapour pressure of liquefied petroleum gases.
BS 5045 Transportable gas containers.
BS 5500 Unfired fusion welded pressure vessels.
BS 2869 Petroleum fuels for oil engines and burners.
BS 799 Oil burning equipment.
BS 5410 Code of practice for oil firing.
BS 3300 Kerosine (paraffin) unflued space-heaters, cooking and boiling appliances for domestic use.
BS 4876 Performance requirements and test procedures for domestic oil-fired burning appliances.

23

Industrial Fuels

By G. S. PARKINSON

INTRODUCTION

The term 'industrial fuels' comprises any liquid petroleum fuel used for production of heat in steam or hot water raising, in furnaces, or in gas turbines for industrial purposes.

In practice almost all the applications considered here relate to fuels in the UK complying with the requirements of British Standard 2869: 1983 'Specification for Fuel Oils for Oil Engines and Oil Burners for Non-Marine Use'. Within that specification we shall be almost exclusively concerned with Class D (commonly known as gas oil from an old and now obsolete use to make or enrich town gas); and with Classes E to H grades of residual fuels, often called 'black oils'. Other classes in the Standard are used to a limited extent in industry; for example, Class A1 and Class A2 diesel fuels. Diesel engines used in industry are, however, dealt with separately in another chapter of this book. There is another major use of fuel in industry outside the standard requirements: refinery fuel. It is common practice for refineries to burn the less marketable fractions from the refining processes as fuels for the process units, and in the UK in 1981 for a crude throughput of about 78 million tonnes some 6 m tonnes was so used. The facility with which these sometimes intractable materials, often very high in sulphur and other undesirable materials, can be utilized should perhaps provide some reassurance to those using the more highly refined products supplied to industry.

Whilst it is convenient to use BS 2869 as a yardstick, most oil suppliers have their own marketing specifications which set down more stringent limits in respect of some properties, or extra requirements in the case of others. Specifications which are broadly similar to BS 2869 exist in almost all industrialized countries, for example ASTM D396* in the USA.

Since the last edition of *Modern Petroleum Technology* appeared in 1973, the amount of fuel oil consumed by UK industry has declined by over 50 per cent. A change of this magnitude has had a profound effect on the refining industry and on the applications for which oil fuels are used. It has affected research and development into new burner design. This massive reduction has come about from three factors, all arising from the phenomenal increase in crude oil prices that has occurred since 1973. Economic recession which now appears endemic in the western world, substitution of oil by natural gas and to a lesser extent coal and nuclear power, and fuel economy measures. An added factor is the disproportionate decline in energy use in the steel and engineering industries which are energy intensive, and the continuing shift to a less energy demanding, service industry, economy.

* References to ASTM are to test methods and specifications published by the American Society for Testing and Materials.

All the evidence is that this decline in fuel use will continue, although on a smaller scale. Energy use in total is not expected to grow very much in the UK, even when the economy improves. Coal may make a gradual comeback but this will depend on many factors—capital investment to replace existing oil-fired boiler plant, much of which is far from obsolete, an infrastructure to handle and distribute coal and remove ash and, not least, a viable price differential between coal and oil based on thermal parity. Coal could also be favoured if and when the theory of the fluidized bed combustion process is translated into effective reality.

SPECIFICATIONS FOR INDUSTRIAL FUELS

'The word specification is one of the most overworked and misconstrued terms used in the oil industry.' These words, taken from the 1958 edition of one of the best books ever published on the subject, *Oil Fuels* by Shell Petroleum, are as true today as they were then.

A specification exists to give the user guidance on the choice of a fuel best suited for his purpose and will have been drawn up with the interests of all the various parties in mind. It is no good setting limits such that the fuel will not perform satisfactorily in all the different makes and types of equipment for which it is intended, nor to produce a quality for which continuity of supply cannot be guaranteed. These can be conflicting requirements as will be seen later. The British Standard for Industrial Fuels has taken into account all these considerations. The items included in BS 2869 and the limits set for them have been arrived at after discussions between representatives of oil suppliers, equipment manufacturers, various user bodies, and local authority and government departments. The final draft of the Standard (it is revised completely about every ten years) is sent out for public comment to interested parties, and foreign standardization organizations. Modifications are made in the light of the comments received.

There are also specifications made for purchasing purposes by large industrial organizations, the electricity supply industry for instance, or government departments. These are also usually more restrictive in some respects than the British Standard, but the latter remains the yardstick for the basic quality requirements of industrial fuels needed for satisfactory operation of oil-fired equipment.

Distillate Fuels Specifications

The principal distillate grade for industrial applications is Class D or gas oil, and is synonymous in most but not all respects with Class A2, diesel fuel. As well as use in the lower thermally rated industrial heating plant, Class D fuel is also used in commercial and domestic applications.

Gas oil is made up of hydrocarbons having boiling points between about 170° and 370°C. Traditionally gas oils have been predominantly paraffinic hydrocarbons, but with changed refinery patterns they may in the future contain more aromatic hydrocarbons derived from cracking and similar processes. Modest treatment of the gas oil fraction may be needed to improve the colour or perhaps to remove sour sulphur compounds or reduce olefins. It

may sometimes be necessary to reduce the inherent sulphur content of the product, for example by hydrofining (see chapter on Refining) to make a product which conforms to requirements set by environmental legislation. Table I gives the specification requirements in BS 2869 for Class D fuels, and also typical figures for those properties.

Residual Fuel Grades

The four residual fuel oil or black oil grades in BS 2869 are differentiated from each other by viscosity. Classes E, F, G, and H are also known as light, medium, heavy, and extra heavy fuel oil. National standards in other countries may specify a different number of grades and viscosity limits.

The black oil grades are made up of residues remaining from distillation and ancillary processes which have then been cut back with high boiling distillate to meet the finished product specification requirements. Heavy gas oils obtained from cracking processes primarily for motor spirit production are particularly good for cutback purposes as they are highly aromatic. The viscosity of residues can also be reduced without the need for so much diluent by a process known as visbreaking, which uses a mild thermal cracking treatment. The finished blend of fuel oil may contain a number of components obtained from different sources. Residues from crudes differ considerably in sulphur and heavy metal content, and specification requirements must be met by blending, since chemical processing to reduce undesired components would be quite out of the question, in economic terms, for residues. Residual fuels can thus vary significantly in the amount of some impurities they contain. The maximum limits of the specification must reflect this extreme situation and can make the product seem worse than it is. Fortunately, North Sea crudes, which are now being processed in increasing quantity, are low in both sulphur and metals.

Fuel oils are blended usually in 10–20 000 tonne tank sized lots. The components are introduced in the appropriate order into a large tank held, heated and blended, usually by jet or in-line blending. Homogeneity is established from viscosity or density samples taken at various levels in the tank

TABLE I

Property	BS 2869:1983 Class A2,D	Typical figures
Density/15°C (IP 160)*	No requirement	0.83–0.86
Viscosity, mm^2/s (cSt), 40°C (IP 71)	1.5 min 5.5 max	3.0
Distillation, % rec. at 350°C (IP 123)	85 min	90
Flash point, closed, Pensky–Martens °C (IP 34)	56 min	70
Water content, % v/v (IP 74)	0.05 max	0.01
Sediment content, % m/m (IP 53)	0.01 max	<0.01
Ash content, % m/m (BS 4450)	0.01 max	<0.01
Sulphur content, % m/m (BS 5379)	0.5 max	0.4
Copper corrosion test (IP 154)	1 max	1
Cold filter plugging point °C (IP 309)		
Summer (March/September)	0 max	−3
Winter (October/February)	−9 max	−12

* Figure in brackets is test method.

blending process. Make-up selection for components can be computer controlled. As well as viscosity it is also necessary to work to sulphur and sometimes metal limits in the finished blend. The chemical nature of residual fuels is most complex. They are predominantly composed of higher molecular weight components known as asphaltic bitumens. Whitehead has recently given an excellent summary of present knowledge on the subject.* Separation of such bitumen-like fractions is an artificial process which has no relation to their practical use. It is achieved by the use of a paraffinic solvent, into a soluble maltene portion, which contains high molecular weight waxes, and precipitated asphaltenes soluble in benzene or toluene. The structure and proportion of the asphaltenes separated will depend on the crude source and the nature of the solvent. Bitumen type fractions are essentially colloidal in nature, and there are necessary interactions between asphaltenes, maltenes, and resins which are present in them.

TABLE II

Specification Limits and Typical Values for Residual Fuel Oils

(BS 2869:1983 Classes E to G)

Property	E (Light)		F (Medium)		G (Heavy)	
	Limits	Typical figures	Limits	Typical figures	Limits	Typical figures
Density/15°C (IP 160)*	—	0.93–0.95	—	0.95–0.97	—	0.97–0.99
Viscosity, mm^2/s (cSt)/80°C (IP 71)	13.5 max	13.0	35 max	30	85 max	60–80
Flash point, closed, Pensky-Martens °C (IP 170)	56 min	above 70	66 min	above 80	66 min	above 80
Water content, % v/v (IP 74)	0.5 max	0.1	0.75 max	0.2	1.0 max	0.2
Sediment, % m/m (IP 53)	0.15 max	0.05	0.25 max	0.1	0.25 max	0.1
Ash, % m/m (BS 4450)	0.1 max	0.02	0.15 max	0.03	0.02 max	0.03
Sulphur, % m/m (IP 61)	3.5 max	2.0–3.3	4.0 max	2.0–3.8	4.0 max	2.0–3.8

* Figure in brackets is test method.

Whilst the chemistry of fuel oils is of great scientific interest and far from being fully understood, it is fortunately not of significance for proper use of the fuels. The main requirement is that the fuel blend, once manufactured, shall remain homogeneous and not show any tendency to deposit asphaltic material during prolonged storage or on mixing with blends made from different crudes or from other suppliers. Stability tests are used by all suppliers to ensure this. They comprise a form of solvent dilution test on a small sample of oil (see ASTM D2781). In practice asphaltic precipitation from unstable blends is almost unknown, but problems can and will arise if residual coal tar fuels are mixed with residual oil fuels. Nor should the precipitation of wax from fuel be mistaken for the same phenomenon. This is unfortunate when it occurs, but is a reversible process, the wax going back into solution on heating, whereas with asphaltic precipitation the situation is irreversible. This problem is dealt with later.

* 'The Heavy End of the Barrel—Future Trends in Oil Firing' (see Bibliography).

PRACTICAL SIGNIFICANCE OF TESTS IN BS 2869

The tests listed in Tables I and II serve a number of purposes. They may try to simulate some aspect of equipment performance as, for example, the Cold Filter Plugging Test for distillate grades. A basic problem with this type of test is that individual sets of equipment designed ostensibly for the same function can vary considerably in respect to the demands they make on the fuel.

Other tests, such as flash point, are included for safety or legislation reasons or, like water content to limit permissible contamination. Or they enable secondary properties, such as specific energy, to be calculated rather than determined where the latter procedure is tedious or difficult.

The tests listed below are as they appear in BS 2869, not in any order of importance. Test methods are either those specified in the IP Standard Book of Test Methods (IP) or British Standards (BS). British Standard 2000 will eventually comprise all the necessary IP and other methods.

(*a*) *Density* (*IP 160*)

The density of a substance is its mass divided by its volume. It has no immediate relevance to the performance of fuels and is not included in BS 2869. In practice the density of industrial fuel oils at 15 °C falls within a fairly narrow range—between about 0.810 and 0.870 for gas oils and 0.920 and 0.998 for residual fuels. Usually the higher the viscosity of the fuel the higher the density, but this does not invariably follow.

Although densities are invariably reported at 15 °C, they may have to be determined at higher temperatures: 50 °C in the case of residual fuels. Hydrometers corrected for higher temperature density measurement for this purpose are used. Standard tables,* prepared by the API and endorsed by the Institute of Petroleum and the ASTM and other national bodies are available to allow any volume or density measurements made at higher temperatures to be converted back to 15 °C, the reference temperature for oil measurement for fiscal purposes.

It is possible in the future that some of the heavier fuel oil blends may have a density just over unity as a result of use of new crudes or refinery processes. This could lead to problems with removal of water in storage.

(*b*) *Viscosity* (*IP 71*)

Kinematic viscosity is defined as the measure of the resistance to gravity flow of a fluid, the pressure head being proportional to the density. The time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity. The c.g.s. unit of kinematic viscosity is 1 centimetre squared/second, or stoke. The SI unit is 1 metre squared/second, or 10^4 St. The unit most usually used in measurement of the kinematic viscosity of industrial fuels is the centistoke (cSt) which is 10^{-2} stoke.

Dynamic viscosity is the ratio between applied shear stress and the rate of shear and thus a measure of the resistance of a liquid to flow. The c.g.s. unit of

* API Standard 2540/IP 200/ASTM D1250, Volume Correction Factors, August 1980.

dynamic viscosity is 1 gram/centimetre/second, or 1 dyne/second/centimetre squared, known as the poise. The SI unit of dynamic viscosity is 1 Newton/second/metre squared equivalent to 10 poises. The centipoise (cP) is 10^{-2} poise.

Dynamic viscosity is also known as absolute viscosity and may be obtained from the determined kinematic viscosity by multiplying it by the density of the oil at the temperature at which the measurement was made.

Kinematic viscosity is measured by the time taken for the liquid to pass between two fixed marks on a glass capillary tube held in a bath at constant temperature, usually 80°C for residual fuels and 20°C for distillates. Earlier methods involved measurement of efflux time through a narrow orifice in the test apparatus and the names of the measurement units Redwood I and II seconds, Engler degrees, Saybolt Furol, and Universal are not entirely out of use today.

Viscosity is a most important characteristic of a fuel and is used as a basis of grade classification. The viscosity must be reduced to a suitable level for flow and atomization of the oil. This is done by heating using electricity or steam coils. If a special type of graph paper is used to plot temperature against viscosity a straight line is obtained. Fuel suppliers provide these charts and they have lines plotted on them at the maximum specification viscosity of each grade. Conversion from centistokes to other units may also be given on these charts.

If the fuel is to gravitate freely to the suction outlet in the storage tank the viscosity must not exceed 25 poises and tank or outflow heating must be provided as appropriate. For the fuel then to flow through the type of pipework associated with the typical burner system the viscosity must not exceed 6 poises. Further reduction in viscosity is needed to atomize the fuel successfully in the case of residual fuels. Class E fuels may need preheat to 60°C prior to the atomizer and the heaviest, Class H, fuels may require temperatures as high as 150°C. The final viscosity for a residual fuel lies between 18 and 35 cSt, depending on the mode of atomization employed (see below). The viscosity should not be allowed to fall below about 18 cSt as otherwise leakage back through the fuel pump may occur and wear on the moving parts which are lubricated by the fuel will increase. Class D fuels require no preheat prior to atomization and are thus ideal for the smaller installation even in an industrial plant.

For the purposes of classification the viscosity of distillate fuels is determined at 20°C and residual fuels at 80°C as all the wax is in solution at these temperatures and flow is Newtonian.

(*c*) *Distillation* (*IP 123*)

Fuels are made up of many different hydrocarbons and each of these has its own boiling point. Industrial fuels therefore boil over a temperature range but the distillation test is only of significance in the case of Class D distillate fuels and then in respect of the amount of fuel that distils at 350°C, which is the temperature approaching the maximum limit that can be achieved by the standard atmospheric distillation test that is specified (IP 123). There is a specification limit of 85 per cent minimum recovery at 350°C to ensure freedom from significant contamination with heavier fractions.

There are sometimes additional distillation clauses in the specification which have nothing to do with performance but are required by the fiscal authorities to classify the product for purposes of customs duty. The EEC Common Customs tariff imposes such requirements on what it defines as 'light' and 'heavy' oils which are differentiated for fiscal reasons.

(d) Flash point, closed, Pensky–Martens (IP 34)

This is a safety requirement and measures the lowest temperature at which the vapour of the fuel will ignite under the defined conditions of the test. The fuel is contained in a closed cup, and a flame is applied at intervals to a hole in the lid as the temperature is gradually raised. The closed flash point is the temperature at which the vapour just ignites. If the lid is then removed from the cup the temperature may be raised a further 10°–15°C before ignition occurs again. This temperature is the open flash point. It is the closed flash point that is always specified, and it represents the condition when the concentration of hydrocarbons in the vapour over the oil in the cup is about 0.5 per cent.

Flash point should not be confused with spontaneous ignition temperature. This is the temperature of the fuel at which the sample when heated ignites spontaneously without the application of any source of ignition. It varies considerably according to grade and chemical make-up of the fuel, and is usually in excess of 300°C.

(e) Water and sediment (IP 74, 53)

These are adventitious contaminants, not present to any significant extent in the fuel when manufactured, but picked up in traces in the distribution system and during storage. Water can accumulate from a tank 'breathing' in moist air as the fuel is turned over. Water is also soluble in fuel at the low parts per million range, and a Class D fuel can become cloudy if the temperature falls and shed a trace of water.

Sediment is defined as material insoluble in toluene. In practice it comprises small particles of pipe and tank scale and a few fibres. It is important that there should not be too many of the latter as they are light and float in the fuel, eventually collecting on the fine-mesh filters. Thus there is an additional requirement in BS 2869 that the fuel shall be free of fibrous and similar material in quantities sufficient to interfere with the operation of normal equipment. The word 'normal' is inserted deliberately as some storage systems have very fine prefilters of sintered bronze which may block excessively under these conditions.

(f) Ash

The ash of a fuel is defined as the residue remaining after a fuel sample has been heated in a crucible to a temperature of 775°C. Under the standard conditions of test the ash content of a Class D fuel is not measurable (it is usually about 5 parts per million), whilst the ash of even the heaviest residual grade does not usually exceed 0.05 per cent.

The ash is made up of metallic compounds derived from the oil in the natural

state. The metals are principally vanadium, sodium, and nickel, usually in that order of concentration in the fuel, with much smaller amounts of other trace metal elements of a like kind. The vanadium and nickel are an integral (chemically formed) part of the oil, and the sodium comes from traces of salt water carried with the crude.

Although the ash content is very small compared to solid fuels, it has some significance for certain applications which are considered below under the heading of high-temperature corrosion. For the normal use of fuel in standard boilers and furnaces the ash content is usually not of importance, and the amounts present in the fuel never come near the maximum specified values.

(*g*) *Sulphur content* (*BS 5379, IP 61*)

These two methods are used for distillate and residual fuels respectively. All industrial fuels contain sulphur compounds which are inherent in the crude oil. During the refining process for distillate (Class D) fuels some sulphur compounds are removed. Any sweetening process used for light distillates will remove sulphur compounds responsible for bad colour or odour. It may well be necessary to go further and remove some of the inherent sulphur by a hydrogen treatment process in order to meet environmental legislation. EEC Directive 75/716 requires that any Class D fuel used in the Community shall have a sulphur content not exceeding 0.5 per cent, and this will need to be achieved by hydrodesulphurization if the natural sulphur level is not low enough, or if low-sulphur blending stock is not available.

Desulphurization of residual fuels, whilst technically feasible, is not practised on any scale except to some extent in Japan as it is grossly uneconomic. Where environmental legislation requires the use of low-sulphur fuels, either gas oils have to be used or low-sulphur crudes used whose residue will meet the sulphur limit. These are in limited supply on a global basis, although North Sea crudes fall into this category. This subject is dealt with in more detail in the section on atmospheric pollution below.

When the fuel is burnt the sulphur is converted to oxides, and as well as being the subject of concern in atmospheric pollution these can also cause low-temperature corrosion of metals in the combustion system. This is dealt with later.

(*h*) *Copper corrosion test* (*IP 154*)

A Class D distillate fuel distribution system for a boiler or furnace may contain a good deal of copper pipework in contact with the fuel and this test, which comprises heating the fuel to 100°C and measuring the tarnish on a polished copper strip after some hours, limits the corrosive materials that may be present in the fuel.

(*i*) *Cold filter plugging point and low temperature flow* (*IP 309*)

Just as each hydrocarbon in industrial fuels has its own boiling point, so also it has an individual freezing point. Consequently, when a fuel is cooled each hydrocarbon solidifies in turn and comes out of solution as wax. This appears as

a cloud in a transparent or translucent fuel, and as cooling is continued the amount of wax increases until the fuel will only just flow under its own weight in the test apparatus. These two temperatures are called the Cloud and Pour Point of the fuel, respectively. The Cloud Point can be seen with the naked eye in a Class D fuel, but only can be observed in a dark oil using crossed Nicol prisms as wax crystals refract light.

Neither the cloud nor the pour point of an industrial fuel is a good guide to its flow properties at low temperature. It has long been known that fuels can be handled at temperatures well below their pour or cloud point.

For Class D fuel the Cold Filter Plugging Point is now a standard specification test, as it simulates better than any other the actual behaviour of the fuel in equipment at low temperatures. In this test, fuel is gradually cooled and passed through a fine (45 micron diameter) mesh filter using a vacuum of 200 mm water gauge. The cold filter plugging point is the temperature at which 20 ml or less of the fuel passes through the filter in not more than 60 seconds.

The British Standard requires that fuel supplied to the user during the months of October to February inclusive, shall have a cold filter plugging point not greater than $-9\,^{\circ}C$. For the rest of the year the figure is $0\,^{\circ}C$. The winter figure was chosen after examination of weather data from many meteorological office weather stations' daily readings over the period from 1949 to 1978. The two stations that recorded the lowest consistent figures for a populous area were taken as the basis for the limit. At these sites air temperatures of $-8\,^{\circ}C$ and below were found to occur for periods of 4 h duration or longer on only fifteen occasions, and for periods of 8 h duration or longer on only seven occasions during the thirty-year period. This was considered to be an acceptable degree of risk, being frequencies of 1 in 300 and 1 in 650, respectively, for the five months during which the winter grade is supplied.

Whilst there is no fixed relationship between the cloud point and cold filter plugging point the differential will rarely exceed $13\,^{\circ}C$.

It must be accepted that for very exposed locations and with particularly sensitive equipment the probability of trouble occurring can be higher. Winters, too, differ in their degree of severity. Another problem is that these figures apply only to fuel delivered during the winter period, and summer quality material will still be present in customer storage in October when a cold snap can occur. All these factors point to the need for carefully designed equipment, if possible located so as to give some protection from wind and excessive cold. For residual fuels, minimum storage and handling temperatures based on the 25 and 6 poise viscosities are laid down in BS 2869 (Table VI below) or alternatively the pumpability temperature corresponding to these viscosities may be determined for a specific fuel using the IP pumpability test—(IP 230/81). Normally it is sufficient to specify ambient temperature for the storage and handling of Class D fuels, but for exceptional conditions it may be necessary to consider tank or line heating for this grade.

(*j*) *Fuel oil stability*

Blends must remain stable in storage after manufacture and when mixed with fuels of other origin. Stability in this sense means that asphaltic matter must not be deposited.

Although the test is not specified, it is a general requirement of specifications that blends shall be stable. In most methods fuel circulates over a hot metal surface for a number of hours to measure the amount of deposit formed. This is a thermal stability test, e.g. ASTM D1661. There are also compatibility tests involving mixing residual and distillate components, and assessing the results of extreme amounts of ether in the blend.

It is extremely rare for a fuel to become unstable and deposit asphaltic matter, but were it to happen it is not possible to reverse the situation. The matter is sometimes confused with wax deposition. If the temperature of storage is too low wax may deposit from a fuel and this will return into solution, unlike asphalts, if the temperature of the oil is raised and held there.

In the past problems of wax deposition occurred with Class E fuels which are normally stored at near ambient temperatures. Wax had come out of solution and blocked fuel lines. This had occurred because thermal cycling of the oil in storage around about 40 °C had taken place from the heating and cooling of the fuel. With Class E fuels it is important not to use tank heating unless the temperature falls below the normal ambient level.

SOME DERIVED PROPERTIES OF INDUSTRIAL FUELS

The thermal properties of most interest to the user may be calculated from other specification properties with much greater ease, and at about the same degree of accuracy, than they can be determined directly.

In 1929, in a classic study for the US Bureau of Standards, C. S. Cragoe demonstrated that the gross and net calorific value of a fuel could be calculated from a knowledge of the specific gravity, making suitable corrections for the presence of impurities—water content and ash—and for the lower heat content obtained from combustion of any sulphur in the fuel. The Cragoe formulae have been checked on a number of occasions since 1929 to take account of new crude sources, and have always stood the test of time, although a slight modification may be necessary to the constants in the equations in the future as a result of a very comprehensive study of determined versus calculated values made recently by a French group.

The original Cragoe formulae, recalculated into the modern units of density and specific energy, are as follows:

Specific energy (gross) MJ/kg

$$= (51{\cdot}916 - 8.792\rho^2)(1 - (x + y + s)) + 9.420s$$

Specific energy (net) MJ/kg

$$= (46.423 - 8.792\rho^2 + 3.170\rho)(1 - (x + y + s)) + 9.420s - 2.449x$$

where ρ is the density at 15 °C (g/ml), x is the proportion by mass of water (% divided by 100), y is the proportion by mass of ash (% divided by 100), and s is the proportion by mass of sulphur (% divided by 100).

Cragoe also devised a formula for calculating the hydrogen content (H) of a petroleum fuel

$$H = 26 - 15d$$

where d = density at 15/4 °C.

TABLE III
Ultimate Analysis and Specific Energy

BS 2869 Class	Ultimate analysis*			Specific energy MJ/kg	
	C	H	S	Gross	Net
D	86.3	13.2	0.5	45.5	43.0
E	85.5	11.7	2.6	43.4	41.3
F	85.2	11.7	2.8	43.0	41.0
G	85.0	11.7	3.0	42.7	40.7
H	84.1	11.6	3.5	42.4	40.5

* Balance is made up of trace amounts of oxygen and nitrogen compounds and ash.

Grade Selection

Class D fuels are used for space heating, small furnaces, and other industrial processes, also as an industrial gas turbine fuel.

Class E fuels have a wide application for central heating and hot water boilers and some drying processes.

Class F fuels are widely used for general industrial purposes for medium furnaces, and boilers.

Class G fuels are the heaviest commercially available, and are used for the majority of industrial oil applications in boilers and furnaces.

Class H fuels are used only for central electricity power generation where facilities exist for handling the high viscosity.

In Table III typical values for the gross and net specific energy and the ultimate analysis of industrial fuels are listed.

FUEL COMBUSTION

The purpose of fuel combustion is to liberate the energy contained in the carbon–carbon and carbon hydrogen bonds of the hydrocarbon molecules. In the process carbon dioxide, water vapour, and traces of other combustion products are also formed.

The basic requirements for good combustion are proper atomization of the fuel by which the liquid is split up into fine particles or mist, and intimate mixing with just more, but not too much more, oxygen than is necessary for the combustion process to be complete.

Atomization of fuel requires energy and can be accomplished in a number of different ways. These are dealt with in the next section. The combustion reaction is complex and involves a free-radical mechanism, but the simplest way of representing it for heat calculation purposes is as follows:

(1) Carbon + oxygen = carbon dioxide

(2) Hydrogen + oxygen = water vapour

Or in equation form:

(1) $$C + O_2 = CO_2$$

(2) $$2H_2 + O_2 = 2H_2O$$

The quantities required from the relative atomic weights (carbon = 12, hydrogen = 1, oxygen = 16) are on a kilogram basis:

$$12\,\text{kg carbon} + 32\,\text{kg oxygen} = 44\,\text{kg carbon dioxide}$$

$$4\,\text{kg hydrogen} + 32\,\text{kg oxygen} = 36\,\text{kg water vapour}$$

The rupture of the carbon–hydrogen bond provides over four times as much energy as does the carbon–carbon bond rupture; therefore liquid fuels with their higher hydrogen content relative to carbon have higher specific energies than solid fuels whose carbon content is higher. Liquid fuels with a higher hydrogen content were sought, but in practice there is insufficient variation to affect the energy content between fuels.

When the fuel is burned the sulphur compounds are converted to oxides, mainly the dioxide but also to a small extent to the trioxide.

$$S + O_2 = SO_2$$

$$2SO_2 + O_2 = 2SO_3$$

There is less energy from the rupture of bonds containing sulphur than carbon or hydrogen bonds.

The combustion of one kilogram of a heavy residual fuel oil theoretically requires about three cubic metres of oxygen contained in about 15 cubic metres of air at normal temperature and pressure. More than three-quarters of the air is made up of nitrogen which gets a 'free ride' through the system and serves to carry away a good deal of the heat energy. Small amounts of nitric oxide are also formed at flame temperatures.

$$N_2 + O_2 = 2NO$$

This reaction reverses at higher temperatures, but as the combustion gases are quickly quenched by passing out of the appliance they invariably contain a few hundred parts per million of nitric oxide. Whilst this gas is inert and non-corrosive and non-toxic, it reacts slowly in the outside air with more oxygen to give the more aggressive nitrogen dioxide. This aspect is dealt with later.

For combustion to be a practical proposition without creating smoke most industrial appliances need to be run with an excess of air above that required stoichiometrically. The excess is usually from 5 to 20 per cent, and it is bad practice to run at higher levels. The amount of air being used is usually measured indirectly through the carbon dioxide content of the flue gases. Most appliances work with a carbon dioxide level of around 12 per cent.

In some large plants which are well instrumented and equipped with oxygen meters it is possible to work at much lower levels of excess air. This minimizes sulphur trioxide formation.

The atomized particles of oil mixed with air are injected into the combustion zone, and temperatures of 1400°C or more are reached. The fuel boils from the outside of the droplet which collapses. The asphaltic residue in a residual fuel droplet forms an almost spherical and hollow cenosphere by the time the temperature has reached about 800°C. Pores and blowholes are formed connecting to the outside and allowing free access of air so that the coke can burn away. This takes about half a second out of the total combustion time for a particle of about one second. It is important that the flame is not chilled by

impact on a cool metal surface before combustion is complete and that sufficient oxygen is available where it is needed; otherwise black smoke can be formed. As little as 0.5 per cent fuel remaining uncombusted can give an unacceptable level of stack solids. These can be measured using techniques which involve collecting isokinetic samples of flue gases on glass wool filters.

This is a relatively simple description of the combustion process, and for a more detailed account of the chemical processes involved reference should be made to the works in the bibliography. One point is worth mentioning. As a result of studies made over a number of years into the combustion mechanism the Central Electricity Generating Board has found that the trace levels of vanadium present in most residual fuels actually speed up the rate of burn-out of the carbon cenosphere.

There is a fear that the heavier fuels which will be made in the future as a result of deeper cracking will be much more difficult to burn, and that the combustion process may not be completed in the time available. There have been a number of studies on the parameters which best predict combustibility. The best indicator seems to be the soft asphalt content (defined as material insoluble in n-heptane but soluble in hot benzene), although particulate emissions are not closely related to any single physical characteristic of the oil. It has been found that fuels produced by visbreaking processes, now being installed at a number of refineries to maximize light products, are no more difficult to burn than ordinary residuals. This process tends to increase the asphaltene to vanadium ratio.

OIL BURNERS

The function of the oil burner may be simply described: to atomize the oil efficiently and mix it intimately with sufficient air to ensure complete combustion. There are several different ways of atomizing oil. In the process the surface area of the original oil is increased many thousand-fold. The objective of making each oil particle the same size approximately is very difficult to achieve in practice. Burners also once set up will deteriorate in performance and need to be adjusted from time to time.

A burner must be designed to give the heat output required and this often requires more than one in a boiler or furnace. A good deal of art as well as science is needed to produce a flame of the correct shape and size for the combustion chamber, achieving the required temperature in the amount of time available.

(*a*) *Pressure-jet burners*

This is in principle the simplest type and is used extensively, especially for boiler applications. When the burner uses residual grades their viscosity must be reduced to a range of 10 to 25 cSt at the point of atomization, the exact value being dependent on the manufacturers' design recommendations. For Class D fuels no preheat is needed.

The fuel is pumped at a pressure of 14 to 70 bar, again dependent on model and design, through a nozzle from which it emerges as a fine spray with a mean droplet size of 100 to 200 μm. Inside the burner head is a swirl chamber into

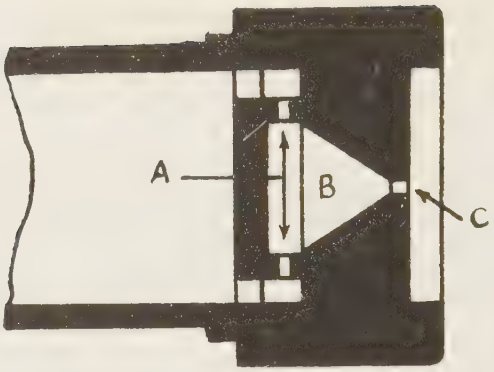

FIG. 1. Pressure jet atomizer. A. Tangential oil inlets. B. Swirl chamber. C. Final orifice.

which the oil first enters through a number of tangential slots or holes. The diameter of the swirl chamber decreases towards the final orifice from which the oil emerges rotating rapidly as a hollow cylindrical thin sleeve (Fig. 1). It then breaks up into a fine spray.

The main advantage of this type of burner is that the output of one or more burners can be increased or decreased merely by changing the oil pressure, but a major limitation is that the oil pressure must be squared to double the output.

Another important characteristic of oil burners is their turn-down ratio: that is the ratio of maximum to minimum flow rates that can be achieved. For a pressure-jet burner it is limited about 1.3:1. Turn-down ratio can be broadened in a number of ways.

Figure 1(*a*) shows a burner in which the excess oil is removed from the swirl chamber by the duct R, and this is used to control the firing rate. A slightly different principle is used in the burner illustrated in Fig. 1(*b*) in which there are two adjacent orifices and control is achieved by circulating oil between them at fixed rates. The design shown in Fig. 1(*c*) is more complex. It has a number of rings by which the fuel flow is controlled, moved by a piston. The piston can be spring-loaded and controlled by the oil pressure, or attached to a rod for

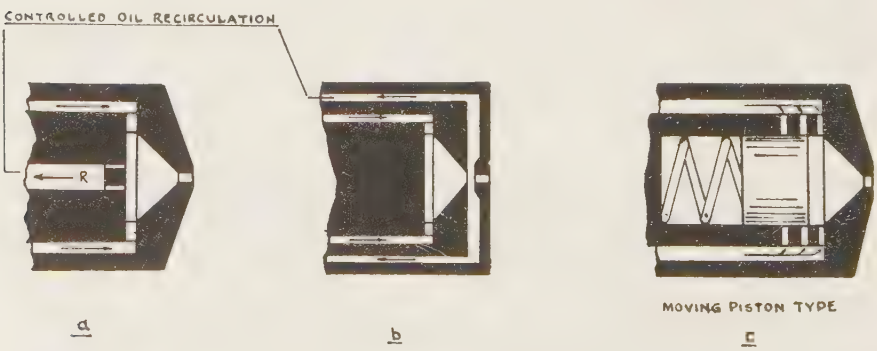

FIG. 1(*a*), (*b*), (*c*). Wide range pressure jet atomizers. Re-circulating type.

mechanical or manual control. A pistonless version is also available, each row of grooves having an individual controlled air supply.

As the momentum of the oil spray is not very great because of oil pressure limitations the pressure-jet burner is used in boilers and not in furnaces. This problem can be overcome to some extent by injecting oil or steam into the root of the oil spray in the so-called pressure-assisted jet burner, but this represents a relatively useless loss of energy. Momentum can also be increased if the jets of oil and steam impinge inside the swirl chamber—the twin-fluid atomizer.

Pressure-jet burners are available commercially with firing rates from 10 to almost 4000 kW per hour. The small orifices in the burner tip can easily become blocked with carbonaceous matter formed by back radiation from the refractory walls of the combustion chamber. They can also be damaged by bad maintenance.

(*b*) *Blast burners*

Blast burners usually employ air at varying pressures as the atomizing medium, but steam can also be used. The oil is torn into fine filaments as it emerges from the orifice and then divided into a fine spray by the impact of the blast of air. The air supplied in this way forms only part of that needed for combustion and is called the primary air.

Blast burners can conveniently be divided into low, medium, and high pressure.

Low-pressure blast burners (Fig. 2) operate at air pressures of up to 20 kN m^{-2}, or 3 psig, and about 20 per cent of the total air requirement is used in the process. For each kilogram of oil this means that 3 to 6 m^3 of primary air is needed. These figures will vary according to the burner type.

A swirl is imparted to the air–fuel mixture by introducing the remainder of the air (secondary air) through registers with swirler plates. The combustion air thus introduced can also be preheated to not more than about 200°C to increase efficiency.

This type of burner is widely used for Class D oils and can be made with turn-down ratios of up to 4:1. Medium-pressure atomizers operate at pressures of 20 to 100 kN m^{-2} (15 psig). Therefore less primary air is needed and about 5 per

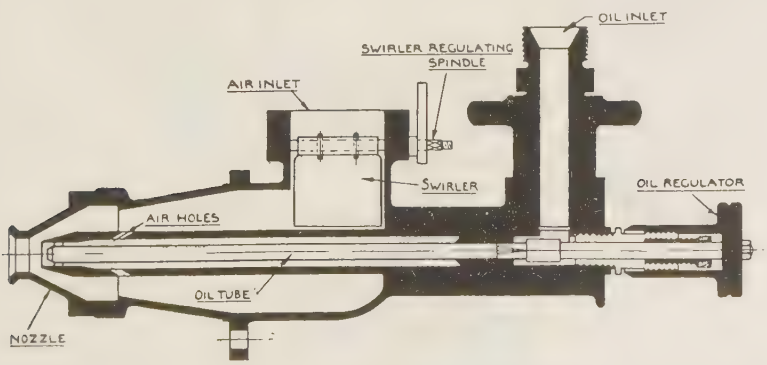

Fig. 2. Low-pressure air burner.

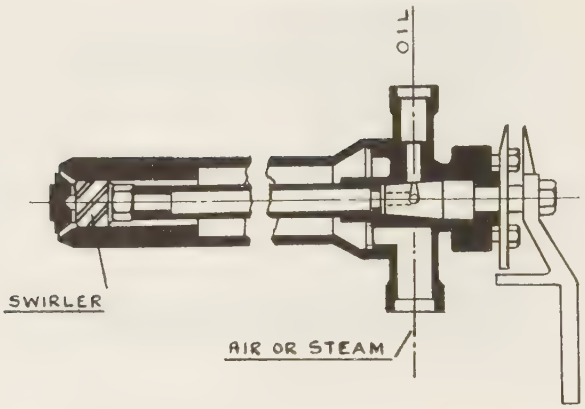

Fig. 3. Compressed air or steam atomizing burner.

cent is customary. In medium- and low-pressure blast burners the air can be supplied by a fan.

High-pressure blast burners (Fig. 3) are mainly used for furnaces and in situations where compressed air is available on site. They operate at pressures upwards of 100 kN m^{-2}. About 2 per cent of the air is supplied at this pressure. This type of burner enables long and shaped flames to be produced which are necessary in furnace work. Steam can be used as an alternative for high-pressure blast burners, but has to be available for start-up, and the energy usage of steam is 20 to 30 times as great as for air.

The toroidal burner, developed by Shell, is a specialized type of blast burner operating on oxygen (illustrated in Fig. 4). The name comes from the toroid shape of the flame which is produced inside a water-cooled case. Combustion takes place outside the burner, and a long narrow or short wide flame can be produced by moving the burner backwards or forwards within the jacket. Toroidal burners achieve flame temperatures of 2600 K and heat releases of up to 10^4 times as great as conventional burners. They were developed to use oil for the rapid melting of steel scrap and non-ferrous metals, and depended on the availability of cheap oil and tonnage oxygen.

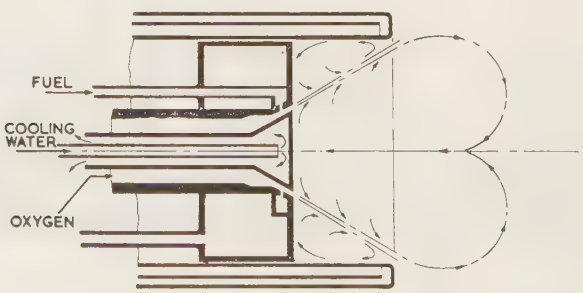

Fig. 4. Shell Toroidal burner using oxygen and liquid fuel: variable flame shape design.

(*c*) *Rotary cup burners*

This is a type of low-pressure air burner using centrifugal force for atomization. The oil is fed into the inside of a hollow spinning cup rotating at high speed. It spreads over the surface as a thin film and is broken up into fine threads and then into coarse drops around 200 μm in diameter. The rotational speed is about 4000 r.p.m. Some 15 per cent of the air is supplied as primary air at an adequate pressure around the burner nose. The cup can be driven by a motor, as in the design illustrated in Fig. 5, or by compressed air.

Rotary cup burners are used in shell-type boilers (*qv*). They have intrinsically low turn-down ratios, but are simple to operate. Performance can be seriously affected if the surface of the disc is damaged or even scratched. The burner unit is mounted on a door that can be swung open for ease of maintenance. Spinning cup burners are available in capacities of up to 3 tonnes/h.

(*d*) *Dual-fuel burners*

Increasingly oil is now used as a stand-by fuel for a plant normally operating on natural gas. Burners must be capable of dealing with both fuels. These are of the

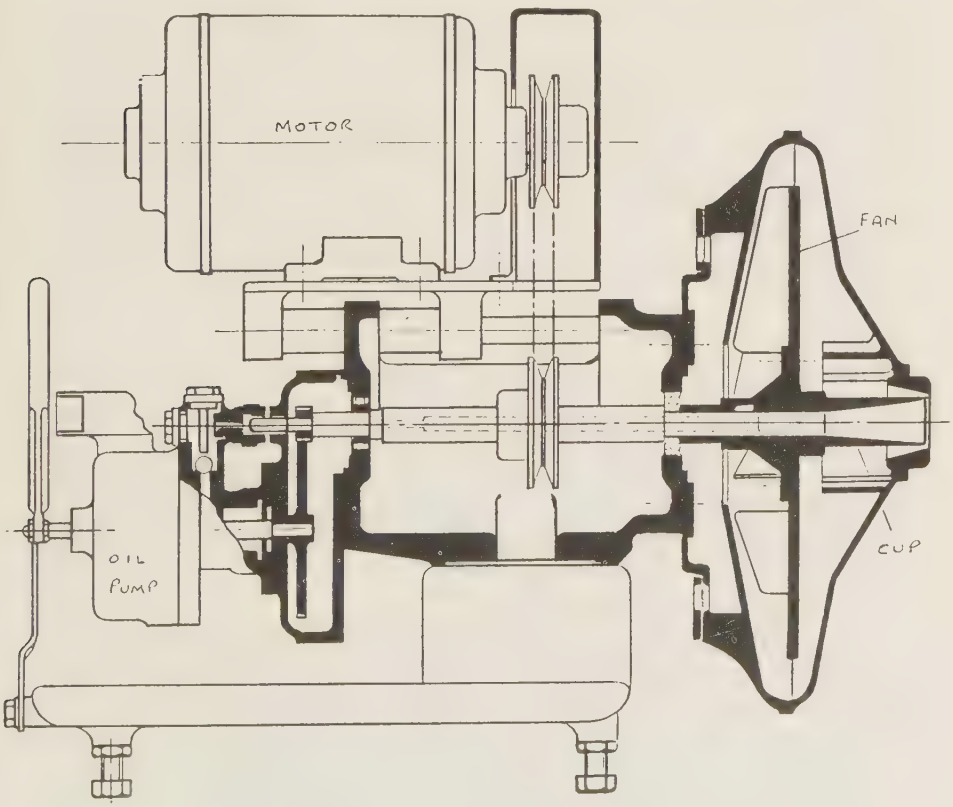

Fig. 5. Motor-driven rotary cup burner.

pressure-jet type with a central oil gun operating on medium-pressure air or steam, and surrounded by a ring of gas nozzles. A gas pilot is fitted to ignite both fuels.

Flame failure devices

All industrial burners are fitted with flame failure detectors, since a failure of this kind could cause a serious explosion. This must be more sophisticated in the case of dual-fuel burners to respond to the characteristics of either flame. These devices use ultra-violet or infra-red flicker detectors. The type of fuel/air control depends on the burner.

Air Control

Atomization is only the first stage in the combustion process, the next is the mixing of the necessary air with the fuel. In air atomizing burners some of that air, up to 25 per cent, has been supplied through the burner as primary air. The remainder, required for combustion, is supplied as secondary air by an opening around the atomizer, either as natural draught induced by the chimney or forced draught from a fan.

The way in which the secondary air is introduced does much to shape the flame. Air directors are used for this purpose. Air passes over inclined vanes which give it a rapid swirl and create turbulence within the combustion chamber. The vortex so created induces a low-pressure zone in the centre, drawing back some of the hot gas towards the atomizer. By admitting a controlled quantity of air around the burner the hot gas can be held back so that the flame can be stabilized at the correct distance from the atomizer.

Another important feature is the throat whose profile governs the degree of mixing. All the various components in a burner require careful design, and must be compatible with each other. Air flow is controlled into the burner with dampers.

Future Trends in Burner Design and Fuel Quality

Burner design has already reached a high stage and the opportunities for further improvement are limited. Fuels in the future may prove less tractable than at present. Some improvement in atomization or air mixing might be possible, but these would involve greater expenditure of mechanical energy; for example, an increase in air velocity of 10 per cent requires an increase in fan power consumption of 30 per cent, so this process is self-defeating. Reducing the viscosity of the oil requires more preheat.

A method that may be used more in the future is to inject about 2 per cent of water into the oil feed to rotary cup burners. This must be done immediately prior to the fuel injection. The addition of water in this way seems to reduce stack solid formation, and this may be more of a problem with the new, heavier oils, at least so it is feared. The vaporization of the water into steam improves the atomizing process which is rather coarse for this type of burner.

When the process is studied using high-speed photography, steam formation is observed which disrupts the fuel prior to the combustion process. The water

also has the effect of reducing the rate of fuel vaporization on account of its higher specific heat and latent heat of evaporation.

The future trends in fuel quality that are forecast as a result of more severe refining are an increase in density, in carbon residue, and a wider variation in asphaltene content.

SOME UNUSUAL BURNER PROBLEMS

Sometimes the presence of very small amounts of inorganic fibrous material in the oil, by weight well within the maximum limit, may cause filter blocking as it can remain in suspension and stop the oil flow. This may be due to no more than a piece of rag that has fallen into the tank and disintegrated, but sometimes it occurs without having an obvious origin. Usually the problem is that the prefilters have too small a surface area for the amount of fuel they are required to pass, or they may be far too fine in mesh size. Some of the filters that have given trouble are very small sintered bronze, of effective pore size only a few microns in diameter.

Another occasional cause of difficulty is the presence of small amounts of salt in the fuel. All residual fuels contain salt, but the amounts are very small and usually kept to less than 50 ppm by desalting at the crude processing stage. Under conditions that have never been fully understood salt dissolved in the very small amounts of water associated with the fuel can come out of solution somewhere in the burner system. This may be connected with the fact that unlike all other common compounds, the solubility of salt in water hardly changes with temperature, and thus salt is almost as soluble in cold water as it is in hot. Salt can come out of solution in the fuel ring main leading to the burner, in the orifices of pressure-assisted burners where the air blast meets the oil, or in a rotary cup burner, although it seems to happen only in models where the cup is over 8 cm in diameter, so it clearly is connected with circumferential speed. A rarer problem is abrasion of orifices in pressure-jet burners by catalyst fines present in the oil which have come from cracked components incorporated in the fuel. These are normally rigorously controlled.

Problems of this kind are very rare indeed, but they are a reminder that fuel quality and equipment design must be considered together, as they will occur only with certain types or makes of burner, whereas the same fuel will give no problems in other types. They also illustrate the point that usually the amounts of contaminants in residual fuels are well within the specification limits, and burner designers have come to rely too much on this always being the case.

CORROSION FROM COMBUSTION PRODUCTS

The next stage in this sequence of fuel use is to consider the effects on materials of the products of combustion from oil fuels. There are two distinct types of corrosion which can occur—low-temperature corrosion from sulphur trioxide and high-temperature corrosion from the fuel ash, but the latter is only of significance in high-pressure boilers and other specialized applications.

Low-Temperature Corrosion

All oil fuels contain some sulphur compounds of natural origin present in the crude oil. Only the corrosive compounds are removed during processing, together with sufficient of the other sulphur compounds in the case of distillate fuels to meet environmental legislation. It is not practicable to desulphurize residual fuels, and the average sulphur content is about 2.7 per cent today.

When fuel is burnt with the usual amount of excess air about 3 per cent of that present is converted to sulphur trioxide which forms sulphuric acid on contact with water. This acid is highly corrosive to metals in dilute solution. The rest of the sulphur is converted to sulphur dioxide which forms the weak, unstable, and relatively non-corrosive sulphurous acid with water. The amount of sulphur trioxide can be reduced, but it cannot be eliminated, if the amount of excess air is reduced to a minimum—2 to 3 per cent. Fine control of this nature is only possible on well instrumented large boilers, and to attempt to run at these conditions on most equipment would produce an unacceptable level of stack solids. There is also evidence that the sulphur trioxide reaction is catalysed by the metal surfaces of the boiler.

Corrosion will only occur where the metal surfaces are below the acid dew-point. This temperature varies somewhat according to the sulphur content of the oil, since it depends on the strength of the acid solution. The acid dew-point temperature is, in effect, the boiling point of that strength acid solution.

The corrosion rate of a metal surface exposed to sulphuric acid is shown in Fig. 6. It will be seen that corrosion is at its greatest when the metal surface temperature is some 20° to 30°C below the acid dew-point—the hump on the curve. As the temperature falls further the corrosion rate at first decreases and then increases rapidly again.

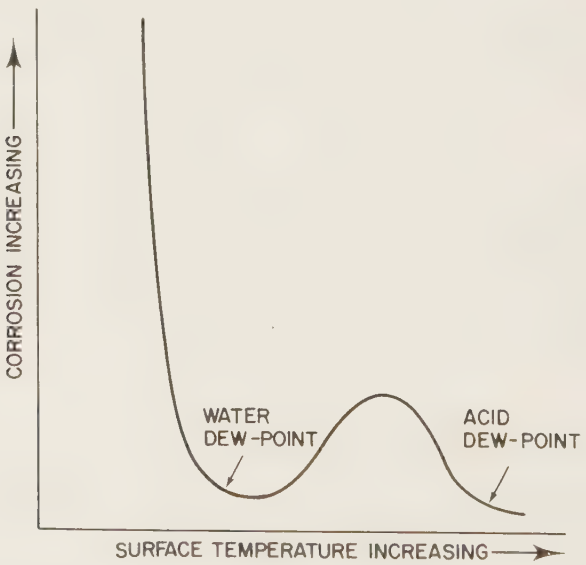

FIG. 6. The relationship between surface temperature and corrosion of steel for flue gases containing SO_2, SO_3, and H_2O.

In the practical situation metal surfaces in the boiler or furnace in contact with the flue gases are never below the acid dew-point long enough for any significant degress of corrosion to take place. Where there can be a problem is in the chimneys and passages leading to them. On older plants many of the chimneys were originally designed for coal firing where the volume of flue gases was much greater for the same heat output. Gas velocities with oil-fired equipment are consequently lower, and temperatures have an opportunity to fall below the acid dew-point, chilled by the massive brick or metal enclosing walls. Corrosion in such conditions will probably be accompanied by smut formation. A smut is an acid agglomerate of carbonaceous particles made up of stack solids and low-temperature corrosion products. Stack solids are usually made up of fine ash particles and cooled at the bottom of the stack. However, if the temperature of the inner surface of the stack is below the acid dew-point (116° to 138°C), which is much higher than the water dew-point (45°C), an acid film layer is formed which is adherent to the wall and acts like a fly paper to collect stack solids which then agglomerate. Corrosion products add to the burden. Changes in the boiler load cause cycling in gas velocities in the stack as a result of which the acid agglomerates are dislodged and carried out of the chimney. They fall within a narrow radius of the origin, depending on atmospheric conditions and create a considerable local nuisance, damaging buildings, cars, and clothes.

The remedy is to ensure that gas velocities in the stack are kept high enough to prevent acid deposition. A steel or aluminium liner can be fitted inside the stack. It is not advisable to use ceramic linings as these can eventually crack under thermal strain and allow gases to leak into the chimney. It is also in the interests of energy conservation to reduce excess air and to make sure there are no leaks of air into the boiler or furnace. Another source of trouble is where one stack is being used for several boilers and off-load plant leaks air into the stack. Sometimes even where all these problems have been dealt with gas velocities are still too low, and at low load inversion of cold air occurs. In this case a truncated cone can be fitted to the top of the stack to increase the velocity, having due regard to the back pressure.

Chimney design is as much an art as it is a science, and has to satisfy the sometimes conflicting requirements of the combustion engineer, the civil engineer, the architect, and the environmental health officer.

Chimney heights for installations are calculated on the basis of the maximum sulphur content and maximum continuous heat input, so as to ensure adequate dispersion of sulphur dioxide emissions. The formula for calculating chimney heights is contained in the *Chimney Heights Memorandum,* issued by the Department of the Environment.

High-Temperature Corrosion

The ash content of residual fuels is small, usually about 0.05 per cent, and it is made up mainly of vanadium and sodium, with lesser amounts of nickel and minute traces of similar metals.

The absolute amounts vary according to the origin of the crude oil. Middle East crudes have around 100 ppm vanadium, whilst North and West African crudes are generally considerably lower, as is North Sea crude, whereas

Caribbean crudes may be much higher. The vanadium is present in the oil as organic compounds, inherently part of the molecule.

Sodium comes from the traces of salt water found with all crudes, and despite desalting processes up to 50 ppm of salt can remain in the residual fuels as marketed.

On combustion the vanadium is converted first to oxides, usually vanadium pentoxide, although several other oxidation states exist and have been found in fuel oil ash. The sodium chloride reacts with sulphur trioxide to form sodium sulphate. Finally, the sodium and vanadium compounds react together to give sodium vanadyl vanadates of which the most usual is the 1.1.5— $Na_2O . V_2O_4 . 5V_2O_5$. Any surplus sodium or vanadium turns up as vanadium pentoxide or sodium sulphate, and a typical fuel oil ash contains all these compounds. When ash deposits and is cooled quickly it remains in a friable form. If it is subject to temperatures over about 450°C it slags and fuses. If held at these temperatures or just below vanadium pentoxide will tend to diffuse to the surface of the slag and can be recognized by its crystalline form.

If the temperature exceeds about 600°C the by now mobile slag becomes aggressive to metal surfaces. The 1.1.5 vanadate melts at 659°C, but there are invariably sufficient lower melting compounds present at temperatures over about 530°C. For the great majority of residual fuel oil users ash is not a problem, but there have been occasional instances with highly rated packaged boilers where for some unexplained reason the ash has built up in some of the tubes of the first or second pass. The upper surface of the ash has fused in consequence of reduced heat transfer and blockage has occurred. This problem has never been associated with any specific characteristics of the fuel, either the sodium or vanadium content or their ratio, and it seems to have something to do with the ability of metal surfaces to catch minute particles of fuel oil ash at temperatures well below their slagging point so that, as in the analogous case with low-temperature corrosion, they act as a fly paper.

In high-pressure water-tube boilers metal stays have to be incorporated inside the very large combustion chamber, and these must be water-cooled to prevent corrosion.

Boilers and furnaces must be shut down periodically and the accumulated fuel oil ash removed. Vanadium compounds are toxic and in this instance sulphuric acid will also be present. Those engaged in boiler cleaning must wear suitable protective clothing and breathing apparatus. Steam lances are used to remove the accumulated deposit, but in some circumstances this may have to be chipped away. Water-tube boiler makers recommend the use of 20 vol hydrogen peroxide solution for cleaning boiler fire tubes which must be taken back to bare metal.

Fuel Treatment and the Use of Additives

It is not surprising that over the years there have been many attempts to overcome corrosion problems by fuel treatment or the use of additives. It is fair comment to say that these have met with limited success, and the more general purpose commercial additives, whose mode of operation is obscure and the sale of which depends on a regular treatment schedule, need to be treated with especial caution.

Perhaps the most obvious treatment is to water-wash the fuel which will remove most of the soluble sodium compounds, but leave the vanadium unchanged. Commercial processes which include centrifugal removal of the wash water are available, but they are only of any economic value in specialized applications where distillate and residual fuels are used for industrial gas turbines.

In theory at least it should be possible to add an alkaline material to the fuel to neutralize the sulphur trioxide, and indeed this can be done. The problems are that it must be injected as a fine powder of alkaline earth (oil-soluble compounds are not feasible) and it doubles, at least, the ash burden.

Problems have occurred in designing a reliable system for the injection of small quantities of a fine powder without clogging. One boiler has been put on the market with a magnesia injection system as an integral part. Recently the CEGB reported on successful trials with a magnesium oxide based additive used in the molar ratio Mg/SO_3 of 2 to 1. A successful injection system to add the material which had a mean particle size diameter of 5 μm was also described. Using this method on power station boilers with outputs of 60 to 500 MW acid smutting problems were minimized and deposit formation was not significant.

Some years ago trials were made on power station boilers using ammonia, but the temperature range for injection was critical—150 to 300°C. Much above this range dissociation can occur and there is also a danger that the glass-like sodium bisulphate could be produced.

Additive treatment has also been tried to overcome high-temperature corrosion and to extend the operating range of equipment using residual fuels. The objective was to add barium or magnesium compounds to the oil which might react preferentially to the sodium with the vanadium and so form a higher melting point and less aggressive slag. Although this was successful in reducing corrosion the problem of deposit build-up on the metal surfaces could not be overcome.

These findings relate to the use of specific additives of known chemical composition employed in calculated quantities to a known rationale. The limited success achieved must make one dubious of the far-reaching claims that are made for many proprietary fuel additives whose mode of action is obscure or unknown. They are to be added at a ratio of about 1 part to 500 of fuel as a preventative and their commercial success depends on regular dosing, without considering whether the problems they are meant to prevent really do occur at all. On analysis many of these products are found to consist almost entirely of an inert oil carrier with a trace of detergent and metal soap.

COMBUSTION PRODUCTS AND THE ENVIRONMENT

We shall now follow the combustion products out of the stack. The main component is nitrogen from the combustion air, 8 to 12 per cent of carbon dioxide, depending on the type of boiler and the amount of excess air, oxygen from that air—possibly up to 5 per cent, a few per cent of sulphur dioxide (although in absolute terms this can amount to many tonnes a day in a large boiler), sulphur trioxide and nitric oxides in the ppm range and traces of fuel oil ash and particulates, with even smaller traces of partial combustion products,

including a class known as polycyclic aromatics. In addition, there will be considerable amounts of water vapour on an equal weight basis to the fuel burned and probably traces of carbon monoxide.

A medium-sized installation using, say, 1 tonne per hour of residual fuel oil, will produce in that time about 1300 m^3 of waste gases at standard temperature and pressure, and considerably more at effluent temperature. They will contain about 1 tonne of water vapour and about 30 kg of sulphur dioxide. Until a decade or more ago there was little concern over the effects of these constituents on the atmosphere. Efforts had been made over almost a century to eliminate smoke produced by the imperfect combustion of domestic and industrial use of coal, and it was only after the Clean Air Acts of 1956 and 1968 that attention focused on the normal combustion products, and by then oil had displaced coal as the major industrial fuel. It is true to say, however, that apart from the sulphur content the amount of the other constituents produced by the combustion of other fuels—coal and natural gas—is roughly the same.

Dealing first with the carbon dioxide, the concern is with the so-called greenhouse effect. Carbon dioxide is fairly transparent to solar radiation, but less so to some wavelengths of thermal radiation. The sun's rays can pass through to heat up the earth, but a significant proportion of the heat is absorbed by the carbon dioxide layer and radiated back to the earth. The present atmospheric carbon dioxide level of 0.03 per cent represents a balance between production and removal by natural processes. There are fears that if the amount of carbon dioxide in the atmosphere increases significantly the temperature of the globe might rise by 2 to 3°C, with significant climatic changes. However, whatever the true position, and the evidence for a build-up is tenuous, the amount of carbon dioxide from oil combustion has decreased markedly in recent years.

There has been more concern expressed over the effects of atmospheric sulphur emissions. A complex series of chemical reactions takes place in the lower atmosphere involving sulphur oxides, ozone, sunlight, and nitrogen oxides, by which the sulphur dioxide is transformed first into sulphuric acid and then, by reaction with ammonia compounds naturally present in the air, into ammonium sulphate which can be precipitated, some say beneficially. Whatever the views on this the national and supra-national authorities have introduced legislation limiting the amount of sulphur that can be emitted into the air, through the establishment of air quality standards specifying permitted annual maximum levels for atmospheric sulphur oxides and combustion particulates. These have resulted in some restrictions on the sulphur content of industrial fuels, notably gas oils. More recently there has been concern over the drift of so-called 'acid rain' which has been held responsible for reduction of fish stocks in Scandinavian rivers, though originating in the UK and Europe. This is still a matter of some controversy, although the results of a survey into drift of acid rain set up by the Organization for Economic Cooperation and Development (OECD) in 1979 gave inconclusive results.

Nitrogen oxides have also become a focus for attention because of their role in atmospheric chemistry, rather than for any proved adverse effects. At the temperatures of combustion a small proportion of the nitrogen in the air and also traces of nitrogen compounds present in the fuel are 'fixed' by reaction with oxygen to produce nitric oxide. This is harmless, but on discharge to the air

TABLE IV

Year	Average sulphur content residual fuel oils (%)	Sulphur dioxide emitted (m tonnes)
1973	2.8	2.18
1974	2.9	2.10
1975	2.9	1.76
1976	2.9	1.61
1977	2.9	1.60
1978	3.0	1.67
1979	3.0	1.65
1980	3.0	1.23

(Source: Institute of Petroleum Statistics).

nitric oxide reacts slowly with oxygen to produce nitrogen dioxide. Some nitrogen oxides are produced from the combustion of all types of fuel and the contribution from oil is small and falling as less oil is used.

It must be remembered that the absolute concentrations of sulphur and nitrogen oxides from oil fuel combustion present in the flue gases is small, and that these substances are also produced by nature. Just as there is a carbon cycle in nature, so also there are nitrogen and sulphur cycles, and the present evidence is that they are still coping well and without difficulty.

To give an indication of the changed situation in recent years Table IV shows the average sulphur content of heavy residual fuel oils in the past ten years and the amount of sulphur dioxide generated by their combustion. The effects of the post-1973 situation are illustrated dramatically in this environmental improvement.

These figures include fuel used for central power generation. If these are excluded the fall in sulphur dioxide emissions is even more marked—from 1.25 m tonnes in 1973 to 0.77 m in 1980. These are the discharges that are made at low and medium level into the atmosphere.

APPLICATIONS OF INDUSTRIAL FUELS

Since the last edition of this book was published the amount of industrial fuels used in the UK has fallen drastically. Table V shows how significant is this change in a number of industries that use considerable amounts of fuel.

TABLE V
Residual Fuel Oil Consumption
(thousand tonnes)

	1973	1981
Steel making	4 295	1 120
General engineering	779	407
Bricks and ceramics	359	115
Paper making	1 305	643
Electricity generation	15 884	4 768
All residual fuels	38 823	15 655

Source: UK Petroleum Industry Statistics.

These reductions have come about as the result of a combination of several factors—a switch to other fuels, especially natural gas, fuel economy measures, the continuing economic recession, and the massive structural changes that have occurred in industry with the replacement of manufacturing by service industries. It is against this sober background that the applications for industrial oil fuels must be considered. Nevertheless, they still have a vital role to play in industry, and any significant move back to coal, however desirable on economic grounds, may prove impracticable on others.

Boilers

'Within the limits of modern knowledge, steam forms the most convenient and economical vehicle for heat for power and process industries.' These words, introducing the chapter on Boilers in the classical book *The Efficient Use of Fuel* which was first published just after the last war, are as true now. What has changed radically in the time is boiler design as boilers were made for coal firing and the vertical cross and fire tube and the stationary locomotive boilers, although successfully oil fired, are now extinct.

Any boiler in which the heat is abstracted by a chamber or cylinder is known as a shell boiler. The Cornish boiler had a single internal flue up to 1 m in diameter. The Lancashire boiler was larger and had two flues.

High heat-transfer rates are achieved on account of the water-cooled surfaces.

Economic boiler

The economic boiler is a modified shell type in which the hot combustion gases traverse the flue tubes to the back of the boiler where they enter the brick-lined or water-cooled combustion chamber. Here the gas path is reversed and the gases pass back through the smoke tubes.

Package boilers

The package boiler designed with heat-transfer rates possible with oil have now all but superseded the older type boilers described above. The limitation of the shell boiler was the pressure at which it could operate, but the use of water tubes instead of a cylindrical shell enables much higher pressures to be used.

These boilers come as a 'package' complete with control equipment and ancillaries mounted as a module for connecting to the services. Package boilers are compact steam generators, flexible in operation and having a high thermal efficiency. A section through a package boiler is shown in Fig. 7.

Package boilers can be dry-back (refractory lined), semi-wet-back (water-cooled except on back) or wet-back (water-cooled).

Typical operating characteristics for a medium rated package boiler are as follows:

Steam output (rating)	8600 kg/h at 100°C
Steam pressure	0.96 MN/m^2 (140 psi)
Thermal input rate	0.38 MW/m^3 (120 000 $Btu/ft^2/h$)

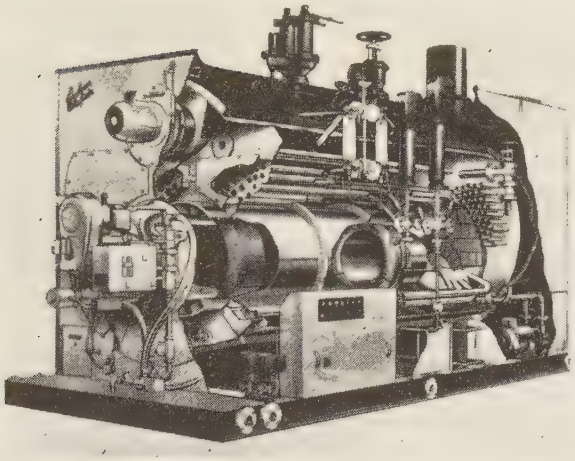

FIG. 7. A fully-automatic package boiler.

The boiler would be fitted with two rotary cup burners, each having a maximum heat output of 0.5 MW/m^2.

Auxiliary equipment would include a 3 hp (2.2 kW) burner motor, a 1 hp (0.75 kW) air fan and a 5 kW oil preheater, delivering oil at 20 psi and 50°C. This gives some idea of the additional heat requirement.

Furnaces

The energy from an oil burner is used in a furnace to heat or reheat process material. Furnaces are classified into the following types:

Melting furnaces—hearth, crucible, or shaft
Sintering furnaces, e.g. cement kiln
Kilns for pottery or brick manufacture
Glass making furnaces
Reheating furnaces
Heat treatment furnaces

There is a considerable variation in the air and control requirements of a furnace dependent on the type and use. Often high-pressure air or steam is used as an atomizing medium, being available on site. It is necessary to exercise very careful control over the composition of the atmosphere in the furnace, and this requires a constant check on air–fuel ratio and monitoring of flame brightness (which is a measure of the oxidation conditions) or of gas composition. These procedures and adjustments are made instrumentally.

Melting furnaces are used in the ferrous and non-ferrous metal industries, although the once dominant open-hearth furnace for melting scrap for steel production is becoming a rarity. The charge is melted by raising the temperature to 1750°C, using water-cooled steam-atomizing blast burners. The use of steam enabled the length and shape of the flame to be controlled in a way not possible with air. The use of oxy fuel toroidal burners lowered directly

into the furnace enabled the production rate in open-hearth furnaces to be increased by over 10 per cent.

Crucible and reverbatory furnaces are used in the non-ferrous metal industry. A reverbatory furnace is one in which the heat from the burner is reflected from a refractory roof.

Rotary kilns several hundred feet long are used to calcine the ingredients for cement. These are fed into the top of an inclined rotating kiln as a slurry in water. Combustion products enter the lower end and the water first evaporates. When the material reaches 900°C carbon dioxide is evolved and heating continues to a maximum of 1500°C, by which temperature a clinker is formed. This is removed and cooled in a clinker chamber with air used as secondary air for combustion, thus utilizing waste heat.

It is, incidentally, common practice for all types of furnace to be fitted with some form of waste heat recovery system, either to heat air, raise steam, or heat water.

Pottery kilns are not now fired with oil on a commercial scale, since atmosphere control and freedom from impurities are vital for high-quality products. Brick kilns are still fired with oil, and the combustion zone is progressively moved along the kiln by igniting the fuel at different ports. The products of combustion pass over and preheat the next layer of bricks to be fired, whilst the previous set is cooled by the air drawn in for combustion, which is itself heated. The kilns can be side-fired, the burner being moved and ports opened and closed successively or, in the simplest form, oil can be dripped with a simple impulse pump into holes in the roof of the kiln.

Glass tank furnaces can hold up to 1000 tonnes of glass. They are fired either over or more usually under the gas ports located in either side and through which the waste gases pass out and the secondary air enters. Firing takes place alternately from each side. Two recuperators, refractory filled, are in tandem, so that as the exit gases are giving up heat to one secondary air is being drawn through the other and heated in the process (Fig. 8). Reversal occurs about every 15 minutes. The best flame control can be achieved by firing through-port, using water-cooled burners which are withdrawn as required.

Refractory on the roof and sides of a glass furnace can slag with the vanadium and sodium in the fuel, and the resulting green black slag falls into the tank and imparts an undesirable green tinge to the product. Although special low-vanadium fuels are available, for quality ware production the tendency now is to use gas.

Reheating furnaces are confined to the metal industries where heating prior to shaping is required. The design and size is specific to the operation, and these furnaces can either be batch or continuous, some suitable method being used in the latter case to move the material. In this type of furnace the aerodynamic properties of the gases and the rate of mixing with air are critical to the final quality of the product and there have been many theoretical studies on flame emissivity. This can be improved by using a luminous flame, and high carbon/hydrogen ratio oil fuels were once sought in an effort to increase the carbon content. The addition of finely powdered coal to the oil was also tried.

Another method of producing a luminous flame is to introduce the secondary air without swirl into the furnace. The injector action of the high-pressure air or steam-atomizing jet draws in the secondary air, and combustion occurs at

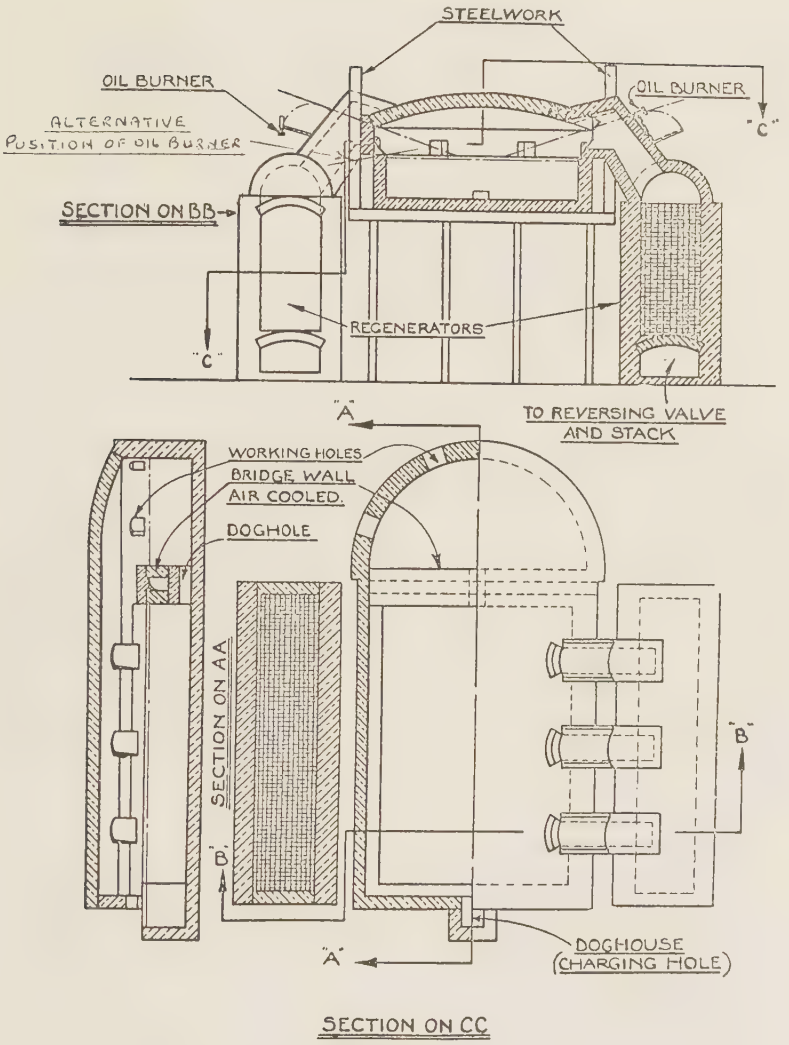

Fig. 8. Diagrammatic arrangements of oil-fired regenerative glass melting tank.

the outside of the spray envelope. The fuel in the centre is subjected to intense radiant heat, and in the absence of air it cracks liberating fine carbonaceous particles which, as they burn, make the flame highly luminous and strongly radiating.

Heat treatment furnaces. Atmosphere control is essential in this type of furnace as the surface treatment of a metal depends on temperature and oxidation state.

Refractory Attack

If the flame impinges directly on the refractory of a boiler furnace slagging or spalling will occur, with damage and often collapse. The sodium in residual

fuels may lower the slagging point of the refractories, especially if they are alumina-based. The vanadium present in these fuels, although itself not directly responsible for the attack, will impart a green-black colour to the slagged material.

If refractory attack has occurred flame impingement is almost certainly the cause, and combustion conditions and the state of burner maintenance require attention.

STORAGE AND HANDLING OF INDUSTRIAL FUELS

Liquid petroleum fuels are a highly concentrated form of available energy: 1 cubic metre of residual fuel oil contains about 42 600 MJ of specific energy, gross.

The most widely used type of tank for storing industrial fuels is welded mild steel. Usually the tanks are cylindrical, although they can be rectangular. They are usually installed in a horizontal position, with a slight rake away from the offtake end so that traces of water may collect.

The minimum recommended net storage is three weeks' supply of oil, on the basis of maximum throughput, with a minimum, for small tanks, of 2950 litres. A large installation will have more than one storage tank. Service tanks are often also installed between the main tank and the appliance. These are of relatively small capacity, but provide a working reserve or a static head.

Storage tanks should be located above ground and not in a position unnecessarily exposed to the elements. They must be surrounded by a catchpit or bund wall sufficient to hold all the oil from the tank securely in the event of accident. Tanks are painted externally, but should not be treated internally.

The following fittings are required:

Oil level indicator—on the tank or remote reading.
Dipstick hole with cover.
Filling pipe—short as possible and free from bends, with gate valve and non-ferrous dust cap.
Vent pipe—equal at least in bore to filling pipe. Fitted at highest point of tank and terminating in 'goose neck'.
Draw off connection—at raised end of horizontal tank with screw-off gate valve.
Drain valve—fitted with screw-off gate valve at lowest point.
Tanks require regular draining prior to fuel delivery.
Manhole—not less than 460 mm diameter, securely fixed and vapour-tight.

Figures 9 and 10 show typical storage tanks for distillate and residual grades of fuel.

Tank Heating

Class D fuels may be stored, handled, and atomized at ambient temperatures. Normally no heating facilities are required, but in exceptional conditions heating should be provided so that in very cold weather the oil temperature does not fall below 10°C.

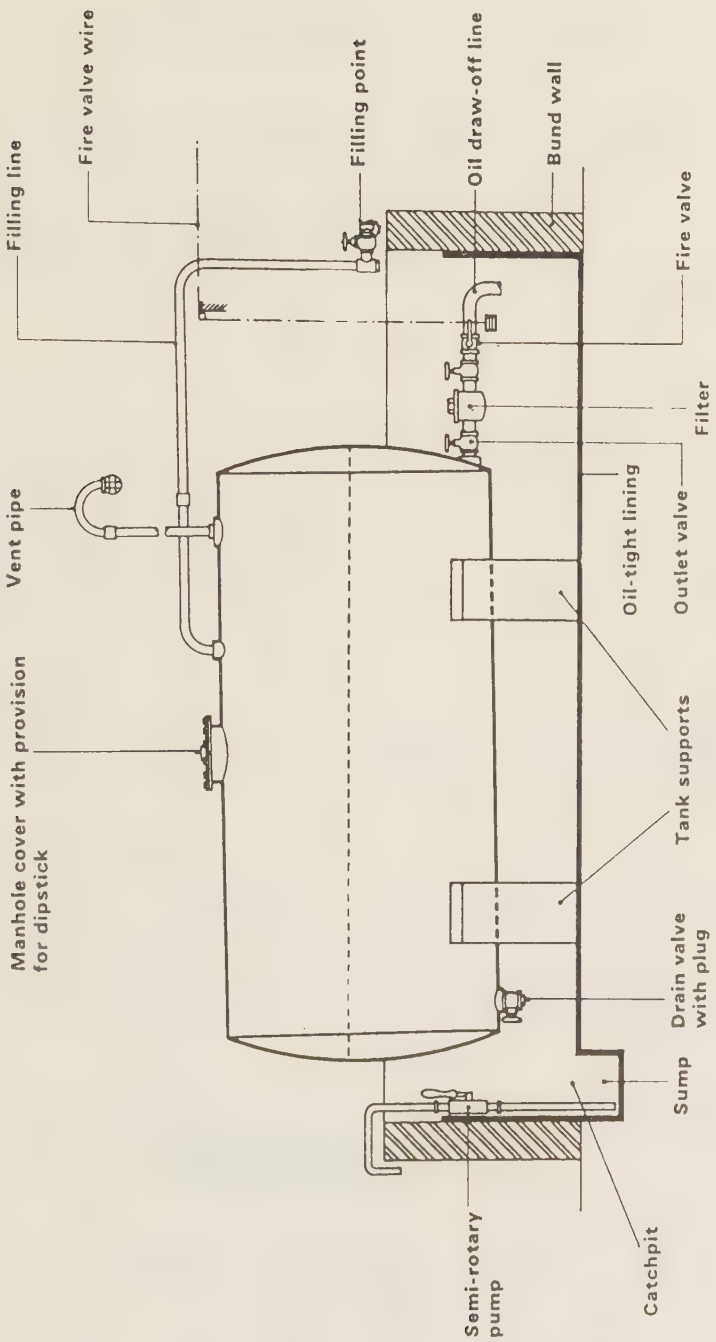

FIG. 9. Storage tank for distillate grades of fuel.

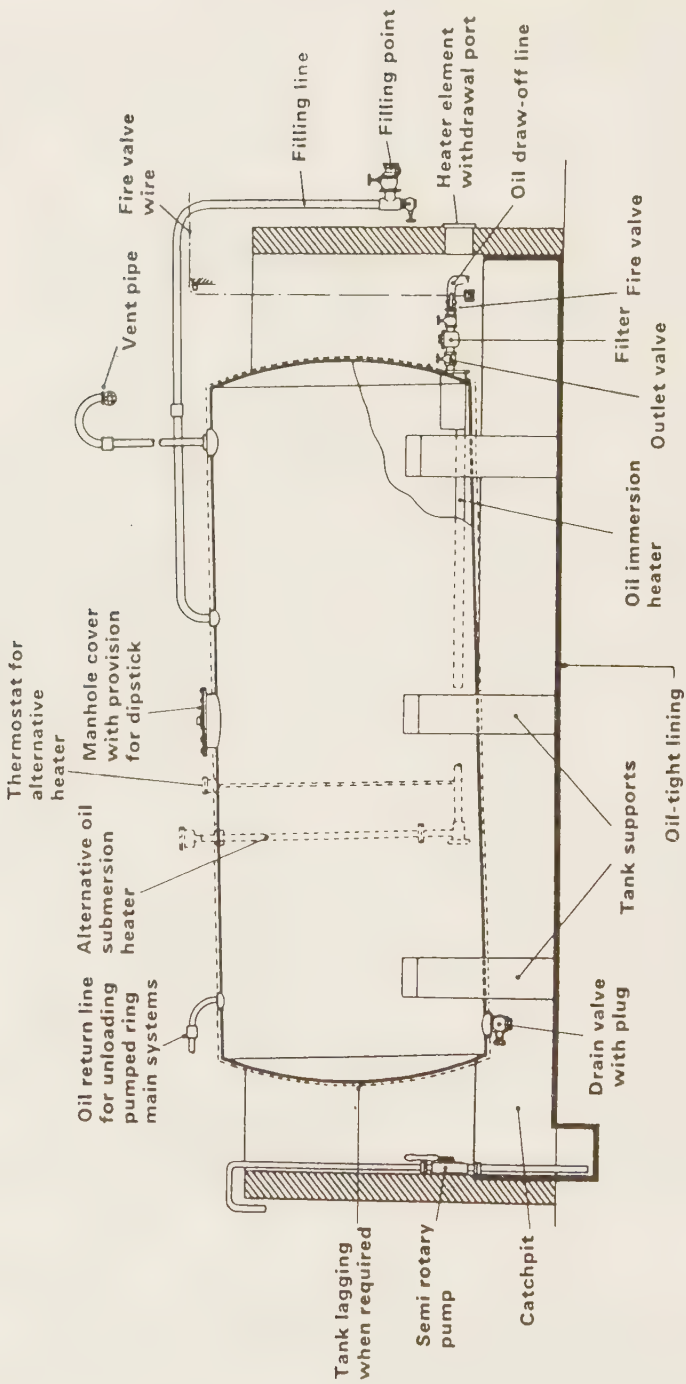

FIG. 10. Storage tank for residual grades of fuel.

Class E, F, G, and H grades require heating facilities. It is not good practice to store oil at unnecessarily high temperatures, and the minimum temperatures in Table VI should not be exceeded by more than about 17 °C, especially in the case of Class E.

The heating requirements for a tank are best determined from heat loss tables provided by the oil supplier who will give much useful information on storage and handling requirements. For example, an exposed tank of heavy residual fuel oil maintained at 40 °C will lose energy equivalent to 300 Wh if unlagged. Lagging reduces losses by about 75 per cent.

Storage tanks can be heated with thermostatically controlled steam coils, hot water coils, or electrical heaters. The mean heat content of a residual fuel is 1.8 to 2.0 kJ/kg °C.

Filtration

Filters must be incorporated in the handling system. A first-stage filter for residual fuels is placed in the draw-off line, and has an equivalent mesh of 2.5 to 0.75 mm. Finer filtration should not be employed at this stage, except for Class D fuels where the first-stage filter can be paper with apertures not less than 0.01 mm. Second-stage filtration is usually incorporated in the burner assembly with an adequate filtration area (to ensure a pressure drop of not greater than 14 kN/m^2), and a nominal aperture of between 90 and 2000 μm, dependent on filtration viscosity.

Fire Valve

A valve which closes the line in the event of a fire is fitted as close to the tank as possible and is usually set to operate at a temperature of above 68 °C.

Oil Handling Systems

A gravity system can be by gravity, pump assisted gravity, or sub-gravity, and is one in which the oil flows directly from the storage or service tank by a gravity feed line. In a sub-gravity system a pump is used to suck oil from a tank.

Ring main systems draw oil from storage and circulate it to each consuming point, returning the balance of the oil to the suction side of the pump or to

TABLE VI
Recommended Storage and Handling Temperatures from BS 2869

BS Class	Minimum storage temperature	Minimum outflow temperature from storage and for handling
E	10 °C	10 °C
F	25 °C	30 °C
G	40 °C	50 °C
H	45 °C	55 °C

storage. Ring mains can circulate hot or cold oil, but the hot oil main offers economies by enabling lower viscosity oil to be circulated through smaller diameter pipes and fittings. The oil is circulated at atomizing temperature. Lagging of pipework and electrical or steam tracing will be necessary to ensure that the temperature of the oil in the pipe does not fall below the minimum handling temperature.

Delivery

Fuel supplies to the customer may be made by road vehicle, rail tank wagon or coastal tanker. Road delivery is most usual and is made in vehicles with capacities ranging from 11 800 to 28 700 litres. Delivery vehicles discharge fuel into storage usually by pump or very occasionally by compressed air at rates up to 1000 litres per minute.

FUEL ECONOMY

No chapter today on oil firing would be complete without some reference to fuel economy which has been practised with greater effect since the massive oil price rises.

The thermodynamic efficiency of a boiler working at normal temperature and pressure is around 70 per cent, and there is little that can be done to improve on this. Heat is lost up the stack, but the hot gases are buoyant and draw in the secondary air. If attempts were made to remove heat from the stack gases not only would the buoyancy be lost and have to be replaced by fan power, but corrosion problems from sulphur trioxide would also occur. Neither are there major achievements in efficiency to be obtained from the combustion process, unless the amount of combustion air used is excessive. Certainly the aim should be to run with the minimum excess air consistent with smoke-free performance, and the boiler or furnace should be tested to detect any leaks of air through faulty refractory or around badly fitting furnace doors.

On the fuel oil storage side lagging will reduce heat loss from tanks. Pipework to the burner should also be as straight as possible and lagged to reduce frictional and heat losses. Remembering that heat losses increase with the power of the temperature difference, storage temperatures should be kept at the minimum consistent with proper flow.

The main savings are likely to be achieved through a careful analysis of the load pattern on the boilers, and optimization of demand between boilers where more than one is used.

Fuel economy is now a major technological enterprise and is best left to experts, who can often produce surprising savings.

COAL OIL DISPERSIONS

Whatever the immediate prospect for a return to coal as a fuel for industrial purposes may be there is no doubt that it will have to come in the longer time scale. The major disadvantages of coal in an age that has become accustomed to oil are its lower specific energy per unit weight, low bulk density, and transport and handling problems associated with a solid material. If the coal is finely pulverized it behaves in many ways as a liquid and some of these disadvantages are reduced. Pulverized coal cannot, however, be burnt at rates of less than

1 tonne/h, because of safety and ignition problems. A possible solution is to disperse the finely-divided coal in a heavy oil when it can be handled as a liquid, but with the reduction in oil consumption of up to 60 per cent.

Dispersions of coal are manufactured by reducing the particle size of pulverized coal by ultra-fine grinding to 10 μ. Surprisingly, the first attempts to use coal/oil mixtures were made over 100 years ago, and there were commercial trials between the wars. Some twenty years ago BP experimented with the use of coal/oil mixtures for blast furnace injection, but it has needed the economics of the continuing oil situation to kindle interest in what is a technically feasible proposition.

Research on the manufacture and use of these mixtures is being undertaken at the University of Surrey for BP and at BP's research laboratories.

Stable coal/oil dispersions have been prepared using a variety of fuel oils from Class E to H in viscosity. The coals used have been bituminous, sub-bituminous, and a lignite. The ash content of the mixture ranged from 2.7 to 26.4 per cent, and the sulphur content up to 4 per cent. Water contents were from 0.8 per cent to 17.5 per cent. Clearly these fuels are quite different from oil in their physical characteristics, but no difficulty was found in burning them using a standard low-pressure air burner. All lines had to be short, trace heated and lagged, and the choice of a displacement pump and steam preheating provided the answer. Preheat temperatures were found to be crucial to atomization and fuel stability. It was also necessary to use a modified form of the internal mix burner atomiser tip.

The flames from coal/oil dispersions are rather longer than those from oil itself due to cenosphere formation. It is not easy to burn these out completely, and it may be necessary to derate burners to allow this to be achieved. Most of the ash passed up and out of the stack.

There are a number of problems with coal/oil dispersions that still need investigation and are concerned with the effect on wear and erosion of handling equipment and fuel systems in the burner, combustion, and emissions. The work is sufficiently promising for BP to have taken the decision to construct a plant which will produce 100 000 tpa of stable coal/oil dispersions. These can be made without the necessity of incorporating a stabilizing additive into the blend. It could well be that this fuel will have an important role to play by the time the next edition of this book is produced.

INDUSTRIAL GAS TURBINES

The industrial gas turbine using oil has suffered a severe setback since the 1973 oil price increases.

The principle of operation is to use the heat energy from a combustion process directly, with the combustion products driving the rotor blades of an impellor connected to a compressor or electrical generator. By this means higher thermal efficiencies are possible than with boilers, but these are limited by the ability of materials to resist corrosion at high temperatures. Special nickel/chromium (Nimonic) alloys for rotor blades, which are the most vulnerable areas for attack, have been developed, but even so blade life is limited, as are operating temperatures. Rotor blades usually operate at red heat—around 700°C.

At these temperatures any chloride present in the air or the fuel can cause unacceptable pitting corrosion. Turbine sets operate on Class D fuel, but although the fuel as delivered to the customer may be clear and bright in appearance—this is a general requirement for all gas oil and ensures the absence of any free water—it may still contain a few parts per million of dissolved sodium chloride contained in fifty or a hundred parts per million of water, no more, dissolved in the oil. These very small amounts of contaminant are carried from the crude oil through the refining process. Some types of gas oil are more prone to hold traces of water, which may be shed in part if the oil falls in temperature producing a haze. It is not feasible to remove all the salt and water at the refinery, and amounts of this kind could be picked up during transport to the user. They are of no consequence in any other application.

Most fuel specifications (including an ISO specification for industrial gas turbine oil fuels now being prepared) lay down limits for metallic contaminants 'at the fuel inlet'. The ISO requirements will be 0.5 mg/kg (ppm) maximum, each, for vanadium, sodium plus potassium, and calcium. These levels can be achieved by an elaborate system of water washing and centrifuging the fuel immediately before it enters the reactor, but such treatment is costly, although it prolongs the life of the rotor blades to acceptable limits.

Adequate fuel filtration facilities are also needed. The larger turbine units were designed for aviation use to operate on a kerosine fuel subject to special handling requirements to eliminate every trace of contaminant. Gas oils are more viscous materials, and it was found that even the cleanest could contain 5 to 10 ppm of particles of micronic size in suspension which blocked the pores of the aviation-type filters very quickly. The answer was a two-stage filtration system.

There are also a range of turbines designed specifically for industrial use made by a number of different manufacturers. At least one is for use on residual fuel oil, but the sodium and vanadium in the fuel ash limit the temperature of operation and hence the efficiency. Some success with an additive which increases the sticking point of the semi-molten ash has been claimed, but although this reduces corrosion of blades it can build up deposits to an unacceptable level.

The future of industrial gas turbines will be mainly where gas is available for a fuel at the right price. Oil can only be the fuel of choice in special circumstances—oilfields, etc. The units in the UK central generating network, each capable of up to 55 MW output and with the ability to come on service at a few minutes notice for peak load generation, are now virtually unused. Smaller (18 MW) units are used in power stations for stand-by emergency start-up purposes.

SUGGESTIONS FOR FURTHER READING

British Standards for Oil Fuel and Oil Fired Boilers

BS 2869 Specifications for Petroleum Fuels for Oil Burners.

BS 799 *Part 3* Automatic and semi automatic atomising burners up to 36 l/hr and associated equipment.

Part 5 Oil Storage Tanks.

Part 6 Safety types and safety control and monitoring devices for atomising oil burners of monoblock type.

BS 5410 *Part 1* Oil Firing: Installations up to 44 kW output for space heating and hot water supply purposes.
Part 2 Oil Firing: Installations of 44 kW and above output for space heating; hot water and steam supply purposes.

General and Fuel Efficiency
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The Efficient Use of Energy. Institute of Energy, 1975.
The Efficient Use of Fuel. HMSO, 1958 (for historical picture).
Technical Data on Fuel. London, British National Committee, World Power Conference, 1978.
Liquid Fuels. Williams and Jones. Pergamon Press, 1963.

Future Trends in Fuel and Equipment Design
The Heavy End of the Barrel—Future Trends in Oil Firing. Proceedings of Symposium in November 1981, South Coast Section, Institute of Energy.

Corrosion and Chimneys
Mechanism of Corrosion by Fuel Impurities. Butterworth, 1963.
Chimney Heights Memorandum (3rd Edition). Department of Environment.
Chimneys for Industrial Oil-fired Plant. BP Oil.

Environmental Aspects
Pathways of Pollutants in the Atmosphere. Royal Society of London, 1979.

Coal Oil Dispersions
A. Groszeck. Coal oil dispersions—a substitute for liquid fuels. Royal Society of Chemistry, *Industrial Chemistry Bulletin*, 1982, **1** (1), 19.

Statistics on Consumption
UK Petroleum Industry Statistics (produced annually by IP).

ACKNOWLEDGEMENTS

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Marine Fuel Oil

By R. F. THOMAS

HISTORY

It was in 1870 that the *Constantine* sailed the Caspian sea using oil in her boilers to produce steam for propulsive purposes, and a further twenty-four years elapsed until the first transatlantic crossing by the *Baku Standard* was made in the same manner. At the end of the nineteenth century over 22 per cent of the world's merchant fleet were still sailing vessels, and the remainder, with few exceptions, obtained their energy for propulsion from coal. In the intervening period up to the outbreak of the First World War, marine fuel oil started to be increasingly used in merchant ships. Whilst the pioneers had utilized the oil in a boiler, it was during this period that the marine diesel evolved in an ocean-going vessel. The first ocean-going motorship was the *Selandia*, which sailed on her maiden voyage from Copenhagen to Bangkok in February, 1912.

By 1921, 20.65 per cent of the total merchant gross tonnage used oil fuel for boilers, compared to only 2.62 per cent in 1914, whilst oil in internal combustion engines had risen to 2.0 per cent from 0.47 per cent. The significant change was that then only 72 per cent of the tonnage required coal, compared to 89 per cent in 1914, and the remainder of the tonnage was made up of sailing ships.

In 1921, practically every motorship afloat ran on what was known as diesel oil, whilst oil-fired steamers operated on that grade of fuel known as fuel oil. The difference between the two grades was considerable, as the former was a distillate fuel, whilst the latter was a residual fuel, often referred to as boiler fuel.

It was not until 1947 that a full account of an endeavour to burn boiler fuel, namely residual fuel, was given to the Institute of Marine Engineers. This account was followed by others in the next few years. Shipowners were anxious to change existing vessels to burn residual oil, and were similarly insistent in ordering new vessels capable of burning such fuels. The fuel generally available, with the possible exception of the Americas, was of fairly consistent quality and gave few problems. The era of king coal was over as shown in Fig. 1, and the start of the establishment of the motorship to its present (1982) supreme position is shown in Fig. 2.

The oil being used by the pioneers at sea in the nineteenth century was in fact crude oil which had not been subject to any refining process, whilst in the early part of the twentieth century practically all the marine fuel oil was produced by straight distillation of crude oil, the residue being marketed for steam raising purposes.

By the early 1950s catalytic cracking plant had been installed in many refineries in order to meet the increased demand for gasoline. The result of this process, besides producing gasoline components, is 'cycle' oil. This 'cycle' oil is a valuable fuel oil component, since in addition to its property as a cutter

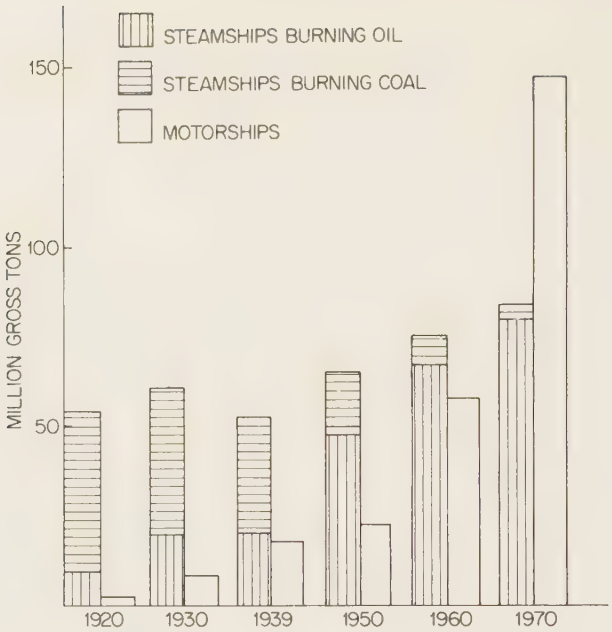

Fig. 1.

stock, its chemical nature makes it a good stabilizer for asphaltene-containing residues.

In the 1970s refinery techniques started to be modified by the introduction of secondary refining processes such as visbreaking. This process increases the middle distillate yield, and consequently results in a small proportion of residue.

The present situation is very complex because the variation of product demand in individual countries is extremely wide, and these wide variations cannot be accommodated by crude oil selection alone because of demand

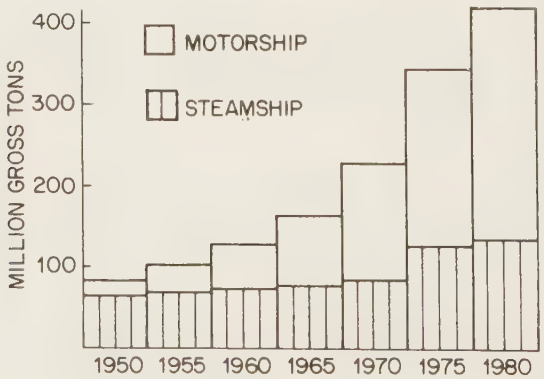

Fig. 2.

volume requirements. Further, within any single geographical area several crude oil sources are used, and numerous refinery process configurations are employed. The result of this is that fuel for the marine market on a world-wide basis is subject to considerable variation in its properties. Whilst this has basically always been the case, the variations today can be more pronounced than they have been in the past. Although the marine fuel oil market only accounts for 4–6 per cent of the barrel, it is still a significant market for the major oil supplier. Marine fuel oil provides the energy to transport the trade of the world by sea, and more tonne-miles are covered in this manner than in all the other means of trade transportation combined.

MARINE FUEL OIL CHARACTERISTICS

Terminology

Within the marine industry both distillate and residual fuels are used, and at present the various grades of fuel are referred to by different names depending on the terminology of the supplier.

In some smaller vessels, and for use in the auxiliary engines of some larger vessels, gas oil is used. This grade of fuel is marketed under various names including Bunker Gas Oil and Marine Gas Oil. Such a fuel is a light distillate, and is a clean fuel in that it does not contain any residual fuel. On the other hand, diesel fuel may contain a small amount of residual fuel, and is known as Marine Diesel Oil or Marine Diesel Fuel.

For residual fuels various names are used by suppliers for this product, and include the terms Bunker C Fuel, Heavy Fuel Oil, Bunker Fuel Oil, and Marine Fuel Oil. These fuels are the highest viscosity and thus the cheapest residual fuel available at a port. Often a range of intermediate fuels are available which have a lower viscosity than the cheapest fuel available at that port, and are supplied to a stated viscosity. Such products are given different designations depending on the supplier, and include such terms as Light Marine Fuel, Intermediate Fuels, Thin Fuel Oils, and Interfuels. Often the maximum viscosity at 50°C in centistokes is suffixed to the designation. For example IF 180 would be an interfuel with a maximum viscosity of 180 cSt at 50°C.

Viscosity

Viscosity is a measure of the resistance of a fluid to shear or flow, and is measured in centistokes (cSt) with a quoted reference temperature. The methods of reporting in Redwood, Saybolt, and Engler units are now obsolete. In recent years 50°C has been used as the reference temperature, and this temperature has been associated with the classification of fuels as discussed in the section on terminology. In the specification described in a later section a reference temperature of 80°C is used. This increase in temperature has been made to take account of the possible non-Newtonian behaviour of a limited number of heavy residual fuels at 50°C. Each fuel has its own temperature/viscosity relationship, and although oil suppliers publish temperature/viscosity charts, it should be appreciated that these charts are based on averaged data of a large number of representative fuels. As the relationship for any particular

fuel depends on its crude oil source and the refinery processes employed, estimations made from the charts, which may well vary, cannot be regarded as precise. In general, for the lower viscosity fuels the difference is small, but it becomes wider as the viscosity of the fuel increases. A knowledge of the viscosity is necessary for the determination of the heating required for a fuel for transfer purposes, and the temperature range required for satisfactory burning at the injector nozzle or burner.

Density

Knowledge of the density of a fuel is needed for quantity calculations; also its value needs to be known in order to assist in selecting the optimum size of gravity ring for purification. Density does not give a direct indication of fuel quality in isolation, and it should be noted that there is no relationship between density and viscosity for fuels from different crude origins or from different blending components.

Density is an absolute relationship between mass and volume at a stated temperature, and in SI units is expressed in kg/m^3. This gives values of 800–1050 for marine fuel oils. In order to give numbers related to unity, SI only allows two alternatives Mg/m^3 or kg/dm^3, neither of which is particularly familiar. However, the dm^3 is exactly equal to the litre, and the unit kilogramme per litre (kg/l) is most commonly used at present.

Densities are measured over a range of temperatures, usually for convenience at the temperature at which the fuel is stored. The value is then corrected back to 15 °C, which is the reference temperature, and is the one used by most excise authorities. This correction is made by the use of standard tables, and these were derived from density measurements of large numbers of fuels representing world-wide fuel availability. New tables were published in 1980, and these show a slightly different density/temperature characteristic from those used historically. For example, a fuel measured at 40–60 °C that gave 0.990 kg/l at 15 °C by the former tables, now gives approximately 0.991 kg/l by the new tables. This does not represent any change in the actual measured densities, only a change in the correction to another temperature.

Flash Point

The flash point of a fuel is the temperature at which the vapour given off will ignite when an external flame is applied under standardized conditions. Its purpose is to ensure safety from fire risk during normal storage and handling. Lloyd's Register of Shipping first agreed to the burning of oil in a ship classified by them in 1898, and at that time there were no rules for oil burning; each case was treated on its own merits, and accepted, with the proviso that the flash point was not less than 93 °C. This figure applied until November 1901 when the value was reduced to not less than 66 °C. In 1971 a second revision was made to 60 °C, and this is the value for ships classed for unrestricted service. It should be noted that for emergency equipment for machinery external to the main machinery space a flash point of not less than 43 °C is permissible.

Sediment and Stability

Sediment by extraction defines the insoluble residues remaining after extraction by toluene. These insoluble residues are contaminants such as sand, dirt, and rust scale, and are not derived from the fuel. Such a definition and test method are suitable for clear distillate fuels, but are not applicable for residual fuels.

In the process of blending a particular grade of residual fuel, the properties of the blend are determined by the proportion and source of each of the components used in the blend, particularly with reference to stability and sediment.

Stability of residual fuel may be defined as the ability of a fuel to remain in an unchanged condition despite circumstances which may tend to cause change; or, more simply, as the resistance of an oil to breakdown. Conversely, instability would be the tendency of a residual fuel to produce a deposit of asphaltic or carbonaceous matter as a function of time and/or temperature.

Various in-house oil company methods exist for the estimation of stability, which include heater, flocculation, and hot filtration tests. Whilst the consequence of residual fuel oil instability is the flocculation of asphaltenes into 'sludge', there are other far more common 'sludges' resulting from different causes. The most common is an emulsion of oil and water; but, separately or together with this, can be found various combinations of gums, resins, free carbon, sand, dirt, and tank scale.

Traditionally the oil refiners have closely controlled the asphaltene 'sludge' level by use of their in-house laboratory test methods, and these have been based on either filtration or centrifuge techniques. With the filtration technique a sample of fuel is filtered hot through a filter paper or an asbestos mat. On the underside of the filter paper or asbestos mat, a vacuum is applied. From above air pressure at approximately 5 bars is applied to force the sample through the filtering medium. The alternative in-house technique is the heated centrifuge test. This test, however, has been applied mainly to examine the sludging effect of fuel oil and distillate mixed together, where the test sample is of relatively low viscosity and moderate temperature.

At present (1982) a new filtration method is being developed which is simpler than the existing technique. Modification has led to the elimination of applied air pressure, with only vacuum applied below the filtering medium. This test method, known as Total Existent Sediment, will provide a standard method to determine the amount of sludge present in residual fuel, that potentially could be separated at filters and in centrifuges. It is possible that on completion of this test method, further work may be required to take account of the ageing of residual fuel, and this would indicate the potential sediment.

Wax

The *cloud point* is the temperature at which wax begins to crystallize from a distillate fuel, and is seen when the clear appearance turns opaque. For fuels that are 'black', namely containing residual components, the influence of wax is indicated by *pour point*. Although marine diesel oil is sometimes received on a vessel as a clear product, and is generally considered as a distillate, for

the purpose of wax indication it is considered black, as it can be delivered through the same transfer lines as residual fuels. The pour point is the lowest temperature at which a marine fuel oil can be handled without excessive amounts of wax coming out of solution. At a lower temperature the fuel will gel, thereby preventing flow. With the more viscous fuels the temperature needed to reduce the viscosity to pumpable levels is sufficient to avoid all pour point problems. But for vessels using fuels of a low viscosity storage heating may be necessary for wax rather than viscosity handling limitations.

Carbon Residue and Asphaltenes

The carbon residue of a fuel is the tendency to form carbon deposits under high-temperature conditions in the absence of air, and may be expressed as either Ramsbottom Carbon or Conradson Carbon Residue (CCR). This parameter is generally considered to give an approximate indication of the combustibility/deposit-forming tendencies of the fuel. The values in fuels which result from secondary conversion processes such as visbreaking are higher than those from other refinery processes. There is insufficient evidence to suggest that asphaltenes give any better indication than carbon residue of a fuel's combustion/deposit-forming tendencies. From trials it would appear that there is no simple relationship between asphaltenes and combustion performance. It should be noted that the term asphaltene used in the generic sense covers a wide range of the heavier hydrocarbon structures. 'Asphaltenes' used in the normal analytical sense, only defines a certain group of asphaltenes.

Water

Of all the possible contaminants in marine fuel oil water is the most common. Normally the actual level is very low, since every effort is made by the supplier to deliver fuel as dry as possible, and 0.1–0.2 per cent by volume is typical. The ingress of water can come from a number of sources which include tank condensation, heating coil leakage, as steam is the usual heating medium, and also tank leakage.

Ash

The ash value is related to the inorganic material in the fuel oil. The actual value depends upon first, the ash present in the crude oil, secondly, the refinery processes employed, and thirdly upon possible subsequent contamination due to sand, dirt, and rust scale. For distillate fuels the ash level, which is defined as the residue remaining after all the combustible components of the oil have been burnt, is negligible.

The ash constituents from the crude oil are concentrated in residual fuels; vanadium, and other contaminants such as nickel, silicon, aluminium, sodium, and iron, are the usual main contributing components.

Vanadium is a metal contaminant that is present in all crude oils in an oil-soluble form, and the levels found in residual fuels depend mainly on the crude oil source, with those from Venezuela and Mexico having the highest levels. The actual level is also related to the concentrating effect of the refinery

processes used in the production of the residual fuel. There is no economic process for removing vanadium from either the crude oil or residue.

Silicon in conjunction with aluminium on a $2\frac{1}{2}$–3:1 ratio would indicate the presence of particles arising from the catalytic process in the form of complex alumino-silicates, often referred to as catalytic fines. As mentioned earlier this is not a new phenomenon, but a contaminant which has potentially been in marine fuel oil component streams for over twenty-five years. It should be appreciated that this is an expensive material for the oil refiner, and that complex measures are taken for its retention.

Silicon may of course be present in the fuel in other forms such as sand. Similarly, aluminium may be present in very small quantities, having being picked up by the crude oil in subsurface rocks, but it is generally accepted that an indication of aluminium represents the potential presence of catalytic fines.

SPECIFICATIONS

Introduction

For the majority of shipowners, bunkers account for a significant part of the vessel's operating costs. The exact proportion depends upon the type and size of vessel, and the trade in which it is employed. It has long been recognized that the propulsion machinery for large ocean-going vessels should be capable of operating on residual-based oils, as this is fundamentally a question of economics because of the cost difference between marine diesel or distillate fuels and marine fuel oil. The commitment of the marine industry to the use of heavy fuel is now such that it is extremely unlikely that adequate amounts of distillate would be available to enable any significant reversion of the world's merchant fleet back to distillate fuel.

Fuel for the marine market, with the exception of distillates, has been ordered by viscosity. Whilst viscosity is an important characteristic it does not give an indication of the other characteristics of the fuel. With viscosity as the sole criterion for the ordering of marine fuels, shipowners remain unaware of these other characteristics. Similarly, the designers of the machinery and fuel systems are not always suitably informed of the fuel characteristics to which they should be designing.

In 1978, the General Council of British Shipping initiated the setting up of a Working Group to consider the development of a standardized specification for marine fuels. One result of this work was the British Standard: BS MA 100:1983 Specification for Petroleum Fuels for Marine Oil Engines and Boilers, an extract of which is given in Tables I and II. In 1980, the British Standards Institution made a formal proposal to the relevant technical committee within the International Organization of Standardization (ISO) that an international standard for marine fuel should be prepared. This proposal for new work was accepted, and an international Working Group was formed. Although significant progress has been made within the international forum, it was considered necessary to issue a British Standard covering marine fuels as an interim measure, for without a reference standard marine fuels would continue to be ordered by viscosity.

TABLE I

Properties of Marine Fuels. BS MA 100:1982

Property	Class											
	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
Density at 15°C, g/ml, max.	—	0.9000	0.9200	0.9910	0.9910	0.9910	0.9910	0.9910	0.9910	—	—	
Viscosity, kinematic, at 40°C, cSt,* min.	1.50		—	—	—	—		—	—	—	—	
max.	5.50	11.00	14.00	—	—	—		—	—	—	—	—
Viscosity, kinematic, at 80°C, cSt,* max.	—	—	—	15.00	25.00	45.00	75.0	100.0	130.0	75.0	100.0	130.0
Cetane index, min.	45	35		—	—	—		—			—	—
Carbon residue, Ramsbottom, % (m/m), max.	—	0.25	2.5		—		—		—	—	—	
Carbon residue, Ramsbottom on 10% residue, % (m/m), max.	0.20	—	—		—	—		—	—	—		
Carbon residue, Conradson, % (m/m), max.				12.0	14.0	20.0	22.0	22.0	22.0	—	—	—
Flash point, closed, Pensky-Martens, °C, min.	43.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Water content, % (V/V), max.	0.05	0.25	0.30	0.50	0.80	1.0	1.0	1.0	1.00	1.0	1.0	1.0
Sediment by extraction, % (m/m), max.	0.01	0.02	—	—	—	—	—		—	—	—	—
Ash, % (m/m), max.	0.01	0.01	0.05	0.10	0.10	0.15	0.20	.20	0.20	0.20	0.20	0.20
Sulphur content, % (m/m), max.	1.00	2.00	2.00	3.50	4.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Cloud point, °C, max.	−16		—	—	—		—	—	—	—		—
Pour point, upper,† °C, max.												
(1 December to 31 March)		0	0	24	30	30	30	30	30	30	30	30
(1 April to 30 November)		6	6	24	30	30	30	30	30	30	30	30
Vanadium content, mg/kg, as V, max.	—	—	100	250	350	500	600	600	600	600	600	600

* 1 cSt = 1 mm^2/s.

† The word 'upper' does not apply to classes M2 and M3.

TABLE II

Other Properties of Marine Fuels for which Requirements will be Specified when Test Methods are Developed. BS MA 100:1982

Property	Class									
	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
Ignition quality, min.	*	*	*	*	*	*	*	—	—	—
Total sediment, max.	†	†	†	†	†	†	†	†	†	†
Aluminium content, mg/kg, max.	30	30	30	30	30	30	30	—	—	—

* A limit for this property is considered to be important, but no suitable method of test is available.

† A value is to be agreed on the basis of a method which is in course of development; values will be added by amendment to this standard following normal consultations.

Aspects of Specification

BS MA 100 covers twelve grades of marine fuel, and defines the maximum or minimum permissible values of the fuel quality criteria. In practice, the fuels supplied will frequently have many quality points below the maximum and above the minimum. The specification is reasonable, useful, and economic.

For example, it would not be reasonable to include requirements for which there was no technical importance, or which demanded closer precision than is normally possible in commercial testing. The specification of a particular parameter must serve some obvious purpose and contribute to the complete specification. Hence, one would not expect colour to be specified for residual marine fuel, for it would not serve any useful purpose. In being economic the specification is not needlessly restrictive. Thus, the determination of each parameter was made with due regard to the effect on the manufacturing process which, if too restrictive, could lead to an uneconomic price to the user or, because of other factors, very limited availability.

A specification has two distinct functions: to control the quality of the product as manufactured, and to ensure the continued supply of a reasonably constant grade to the shipowner.

The major oil suppliers have traditionally produced marine fuel oil to their own internal manufacturing standards. Also they recognize the use of residual fuel in marine diesel engines, and that there is an obligation on them to regulate the quality of the fuel so that it can be used safely and economically. In theory, this might not sound hard to achieve but, in practice, there is a wide divergence of opinion from different engine builders on the fuel quality limitations that should apply for their engines. Equally, there is wide divergence in the design of on-board fuel-handling systems. The inevitable question, therefore, is whether the ship should be designed for the fuel, or the fuel for the ship. Usually the answer lies somewhere between these two extremes. The major problem facing the bunker supplier today is the impact of secondary conversion processes. These processes are an increasingly essential requirement if refiners are to continue to meet the demand. The main priority of the oil refinery is to maintain flexibility of the refinery product barrel against the consumer needs.

Hence the real problem for the supplier is to weigh the requirements of the refiner against the technical limitations of the particular application. In the ideal world the shipowner wants the maximum quality control at the minimum price: in fact, two diametrically opposed requirements. Also shipowners who trade world-wide need to have reasonably assured access to fuel oil of some defined quality.

The real priority of the engine builders is to match that of their customer, namely the shipowner, and consequently they realize that their engine must burn residual fuels in order to compete in the marine market. Usually this is synonymous with fuel having a widely varying quality and being broadly similar to the product used for steam-raising plants.

Notes on BS MA 100

The *classification* of the various classes of fuel is numerical, as a convenient means of reference, and each class is prefixed by 'M' for marine.

Tables I and II define the properties of the various classes of marine fuels, and in general no attempt was made to define suitability for particular engine systems or particular applications. This course was adopted because of the wide diversity of engine systems and applications. Class M1 is a distillate fuel for emergency purposes, and the parameters meet the international requirements for this type of fuel.

Class M2 is a distillate fuel, and can be compared to what was historically known as marine diesel. Class M3 is composed mainly of distillate with a small proportion of residue, and both classes M2 and M3 can be used in vessels without any storage heating systems.

Classes M4–M12 are residual fuels, with progressively increasing viscosity and wider control limits. For classes M10, M11, and M12 there is no density parameter, and these are fuels for use where there is no requirement for centrifuging. It is likely that some of the fuels supplied to these classes will have density greater than 1.0 at 15 °C. As previously mentioned gas oil has certain applications on some merchant ships, and is not included in this specification as it is already covered in other specifications. When ordering gas oil, particular attention should be given to the pour point characteristics of the fuel, especially for a vessel which trades world-wide.

The specification acknowledges the parameter *ignition quality*, but provides no limits. This is because there is at present no quantifiable test method for residual fuel. The criterion needs to be identified, a test method developed, and agreement reached with all parts of the marine industry. It is considered that it may be some time before a suitable test method is adopted.

In the development of the specification, it was not possible to meet totally all the idealistic requirements of the shipowner and engine builder. This particularly applied to the maximum limits for vanadium and carbon residue with respect to the light intermediate residual class M4. It is appreciated that some shipowners in their quest for economy now operate engines on light residual fuel which were originally designed for distillate grades. Further, it is realized that the remaining service life of such engines may be of the order of ten years, and that shipowners will continue to want to operate such installations on the most economical grade of fuel oil possible. In this case, shipowners

should request at the time of ordering lower levels of vanadium and of carbon residue. The fuel supplier at that particular bunkering station will then be able to advise the availability of such a fuel. Similarly, shipowners who burn a light residual fuel in vessels without tank heating should request at the time of ordering fuel with a low pour point. In making the request they should be mindful of the difficulties in the production of such a fuel.

Specific Energy

Marine fuel oil is purchased by the shipowner to produce heat for conversion into work. Hence, from this viewpoint one would expect to find this characteristic quoted in a specification. It should be appreciated that the statement of a minimum value would be based on other parameters already defined within the specification. The specific energy is not controllable in the manufacture of marine fuel oil, except in a secondary manner by the specification of other properties.

Specific energy can be calculated with a degree of accuracy for normal purposes from the density of the fuel, and the application of corrections for any sulphur, water, and incombustibles (ash) that may be present.

The empirical formulae shown below are quoted in BS MA 100:1983 Specification for Petroleum Fuels for Marine Engines and Boilers.

Specific energy (gross) MJ/kg

$$= (51\,916 - 8792\rho^2)(1 - (x + y + s)) - 9420s$$

Specific energy (net) MJ/kg

$$= (46\,423 - 8792\rho^2 + 3170\rho)(1 - (x + y + s)) + 9420s - 2449x$$

where ρ is the density at 15°C, g/ml, x is the proportion by mass of water (per cent divided by 100), y is the proportion by mass of ash (per cent divided by 100), and s is the proportion by mass of sulphur (per cent divided by 100).

On a world-wide basis the specific energy does vary slightly, depending mainly on the density and sulphur content of the fuel. Since low-sulphur fuel is normally retained for inshore use to meet environmental regulations, the typical sulphur content of residual fuel oil is in the range 2.5–4 per cent. Also the significant majority of residual oil bunkerings are in the range 0.95 0.991 kg/l. Figure 3 shows the relationship between gross specific energy (MJ/kg) and variations in sulphur and density, and for the above constraints the values are within the boundary ABCD. By consideration of the arithmetic mean of the specific energy within the boundary ABCD the variation is ± 1.4 per cent.

This variation is determined from an empirical formula only taking account of density and sulphur. It should be noted that a correction for ash and water may be made by subtracting 0.010 (% ash + % water), where Q is the gross specific energy for the density under consideration at zero sulphur content.

The quantifiable method of determination of specific energy is by the bomb calorimeter, and the accepted reproducibility of the test is 0.40 MJ/kg. Based on the arithmetic mean of the specific energy in the boundary ABCD, the accepted reproducibility is of the order of ± 0.95 per cent.

In practical terms it is considered that for the greater majority of bunkerings there is negligible variation in gross specific energy.

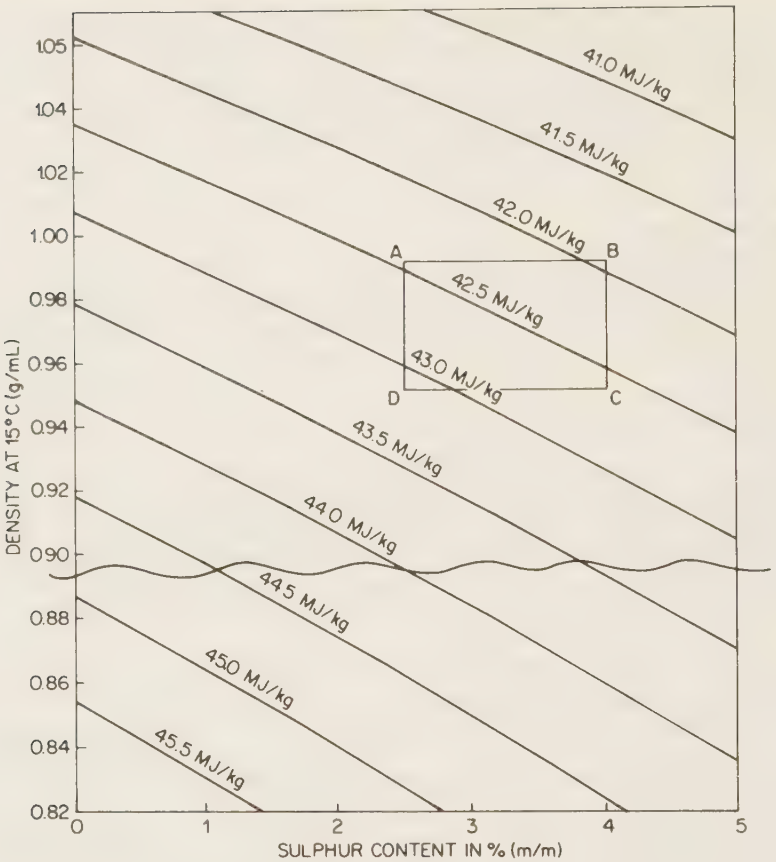

FIG. 3.

Compatibility

The question of sediment and stability within a specific delivery of marine fuel oil has already been discussed, and when two deliveries are blended together there is the possibility of incompatibility. Incompatibility is the tendency of a residual fuel to produce a deposit on dilution, or on blending with other fuel oils. A blend is regarded as being stable if it is homogeneous immediately after preparation, remains so in normal storage, and at no time produces or tends to produce sludge on a significant scale. Under these circumstances the fuels forming the blend can be considered as compatible with each other.

By definition residual fuels are the remainder of the crude oil after the more valuable components have been extracted for the manufacture of petroleum products. The chemical composition of residual fuels depends upon the source crude oil and the manufacturing processes used in the extraction of the petroleum products, and hence it is difficult to define. However, by considering the chief constituents of residual fuels an appreciation can be made of the sludge-formation mechanism. The chief constituents of a residual fuel include asphaltenes, resins, and liquid hydrocarbons. The term 'asphaltenes' used in

the genetic sense covers a wide range of the heavier hydrocarbon structures. Besides being of high molecular weight and high carbon/hydrogen ratios, they may also contain small amounts of other elements, depending on the source of the residual fuel oil. Asphaltenes are believed to exist in residual fuel oil as 'micelles'. The resins can be considered as low molecular weight asphaltenes, and these resins produce true solutions (i.e. molecular dispersions). The resin molecules in an oily medium of a residual fuel are known as 'maltenes', whilst the liquid hydrocarbons are an oily medium of still lower carbon/hydrogen ratio and molecular weight than the resins, which acts as a solvent for the other constituents.

Thus a residual fuel oil is generally considered to contain a disperse phase of asphaltenes complexed with high molecular weight components of the maltenes (resins) and liquid hydrocarbons in the form of a micelle. The continuous or intermicellar phase consists of low molecular weight constituents of the maltenes. In this way one can visualize a general decrease in carbon/hydrogen ratio and molecular weight from the centre of the micelle through to the continuous phase. This is shown diagrammatically in Fig. 4. Although the hypothetical zones are shown separately, in fact they merge with each other, so there is no distinct interface between the micelle and intermicellar phases.

In the conditions shown in Fig. 4 a state of equilibrium exists and the 'micelles' are considered to be 'peptized' (i.e. colloidally dispersed). If, however, the carbon/hydrogen ratio of the maltenes is lowered, say by the introduction of a paraffinic diluent, the resins, which are absorbed on the asphaltenes, are to a certain extent desorbed. This results in the asphaltene particles not being completely surrounded by resins and they are mutually attracted. This leads to precipitation which appears as sludge.

It is considered impracticable to incorporate compatibility in a residual fuel oil specification, as the supplier has no control over the type or origin of the marine fuel oil previously bunkered. The general recommendation is that mixing and blending of fuel from different sources on board ship should be avoided so far as is practicable.

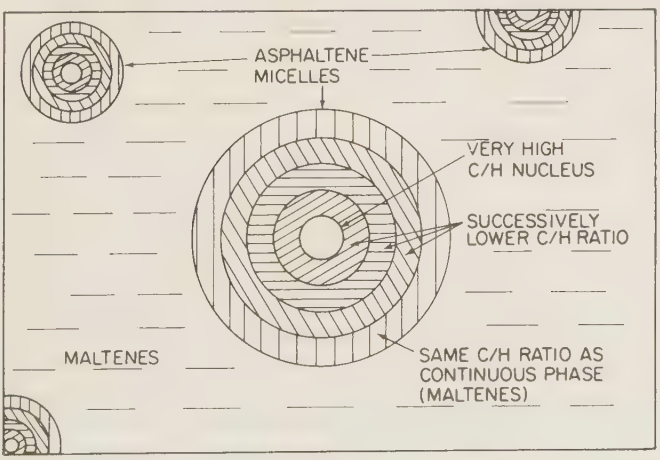

Fig. 4.

TABLE III
Bunker Availability at Three Random Ports

Current grade range	Typical availability		
	Rotterdam (availability)	Durban (availability)	Wellington (availability)
Gas oil	√	√	√
Diesel oil (d)	√	√	
Diesel oil (b)			√
cSt at 50°C			
30	IF	IF	
40		IF	IF
60	IF	IF	
80		IF	
100		IF	
120	IF	IF	MFO
150		IF	
180	IF	MFO	
240			
280	IF		
320			
380	IF		
420	MFO		
460			

TABLE IV
Bunker Availability at Three Random Ports Related to Specification

Current grade range	Typical availability					
	Rotterdam		Durban		Wellington	
	Avail.	Spec.	Avail.	Spec.	Avail.	Spec.
Gas oil	√	Other	√	Other	√	Other
Diesel oil (d)	√	M2	√	M2		
Diesel oil (b)					√	M3
cSt at 50°C						
30	IF	M4	IF	M4		
40			IF	M4	IF	M4
60	IF	M5	IF	M5		
80			IF	M5		
100			IF	M6		
120	IF	M6	IF	M6	MFO	M6
180			IF	M6		
180	IF	M6	MFO	M6		
240						
280	IF	M6				
320						
380	IF	M7				
420	MFO	M8 M11				
460						

Availability

Not all the classes in BS MA 100 are available in all of the bunkering stations world-wide, and it should be appreciated that the heaviest grade of fuel at a particular port varies significantly. This is illustrated in Table III, which shows the typical availability at three random ports based on viscosity, where IF indicates interfuel, and MFO the heaviest grade available. Table IV shows the typical availability in relation to the specification.

Price

The marine market alone does not determine the price of a grade at a particular port. This is set by market forces on the two extreme grades that are used in the production of any grade of marine fuel oil. On the one hand, there is the good quality distillate which is used in the land and air transport industries. The other extreme is the heavy residual fuel, which, besides finding application in the marine industry, is also used for power generation and other industries. These other industrial requirements, which in total are larger than the marine fuel requirement, set the extremes in price. In general, the cost of interfuels at any port is a direct reflection of the price of the extremes at that port. The actual price of marine fuel fluctuates in response to market forces. These fluctuations are probably greater than in most other markets, and result in price differentials between grades which are in no way reflected by any significant quality variations.

Bunker Delivery Note

Historically delivery of bunkers on-board has been accompanied by a bunker delivery receipt, and the amount of information given on a world-wide basis has been variable. While ordered viscosity, together with actual delivered viscosity, density, water, and flash point, has been given in the majority of cases, there have been many omissions. Moreover, the inclusion of additional information has been less frequent. Some shipowners consider that the provision of a bunker delivery note provides confirmation that, by having an analysis of the fuel delivered, this provides assurance that the delivery meets the grade specified. Also, that with knowledge of more of the properties of the actual fuel supplied, adjustments may be made to reduce the possibility of operational problems with the machinery. Similarly, the designers of machinery systems, of whatever type and configuration, also seek information to improve their knowledge of the fuel being burnt.

Provision of a detailed bunker delivery note, available on completion of delivery, is an impracticable solution which could incur significant cost penalties to the shipowner. By the existing infrastructure arrangements at bunkering terminals the required grade is not necessarily prepared before arrival of the vessel, and is sometimes blended just prior to delivery over the ship's rail. Hence any analysis of the fuel could not commence until delivery had started. Even if this was the case, the analytical data would only be a limited estimate of the delivery fuel quality. For a realistic analysis this would have to be carried out after delivery had been completed, on a sample which is representative of that delivery.

Analysis in the laboratory takes several hours, assuming that there is no delay because of the commitment of staff to other work. If there is a laboratory in the vicinity of the bunker terminal, this analysis may or may not cause delay to the vessel's departure. It is well known that such facilities only exist adjacent to a few terminals. Hence the only way an analysis of the delivery could be provided would be by the establishment of, or access to, laboratories with suitable trained staff available on a 24-hour basis at every bunkering station in the world. The cost of such an operation, leaving aside the time for setting up such an infrastructure, would be considerable. This cost would obviously have to be reflected in the price of the product delivered. Also, if the shipowner was insistent on receiving the information prior to sailing, the departure time might have to be delayed. Such a delay would be an additional cost to the shipowner.

For the majority of steamships, the shipboard treatment plant is rudimentary, often consisting only of filters and heaters. It is considered that analysis of the actual fuel delivered would only be of academic interest to the personnel on board, with respect to the efficient operation of plant in their charge. All motorships have some form of fuel treatment arrangement, albeit sometimes only a filter in the case of a machinery system operating on distillate fuel. For those systems operating on residual fuel, the treatment system between the bunker tanks and machinery arrangement depends on that specified by the shipowner at the time of building, or that offered by the shipyard against a standard specification. Whatever arrangement is fitted, the shipowner expects the equipment to be operated by his staff at maximum effectiveness. Given this premise, it is considered that exact analysis before consumption of the fuel, above that already basically provided, will not assist the ship's staff in any material way in increasing the operational efficiency of the plant in their charge.

Knowledge of the fuel's density is essential in the selection of the correct gravity disc for a centrifuge operated as a purifier. The value of the viscosity determines the handling temperature for transfer, and is also necessary in order to establish the approximate temperature for atomization from a viscosity/temperature chart, if automatic viscosity control is not provided. With respect to pour point, it could possibly be argued that knowledge of this figure could be useful in determining the minimum amount of heating required for storage. If the fuel has a high pour point and is stored at temperatures considerably below this, there could be a possible danger of wax deposition. All of this wax may not go back so readily into solution when the temperature of the bunker tank is raised to reduce the viscosity to a level for pump transfer.

A value of the exact sulphur level could, in theory, allow some variation in cylinder lubrication to some engines. However, it is considered impracticable for a ship's staff to change the cylinder lubrication to obtain a variation in the total base number (TBN) of the cylinder oil to match fuel sulphur variations. The amount of sulphur has significance in calculating the specific energy of the fuel by empirical means. In theory, a value of the actual sediment level could be related to the de-sludging interval on a centrifuge.

Knowledge of the exact value of any water in the fuel, as long as it is below the contractual limit, is only of academic interest to the ship's staff, since there is no further action that can be taken once the centrifuges, if fitted, have been set.

Information on vanadium may be of interest if the shipowner has supplied

additives to the vessel for this purpose. As such additives are likely only to be supplied to machinery arrangements which are sensitive to this oil-soluble contaminant, the consequences of variable dosage—with the possibility of underdosage—could be more severe than the theoretical cost saving by dosage reduction under certain circumstances.

On balance, it is considered that shipowners would not wish to pay the additional cost and possibly incur delay in order to have an immediate full fuel analysis on their bunker delivery note. However, some may wish to have an historical analysis made to further their knowledge on the actual fuel received by their vessels. Also analysis of such historical data may possibly provide information that can influence the vessel's maintenance or inspection procedures.

All information on bunkers, and feedback from operating vessels, is useful to machinery system designers, in their desire to produce arrangements to meet the changing needs of the market-place. Historical fuel analysis, with service experience, may help the designer to determine where his research resources, which are not unlimited, should be applied to improve his product. Historical fuel analysis services are available, and it is important that such analytical services are carried out by accepted test methods; also that all the results are quantitative.

Regulations

At present there are two main types of regulation which apply to marine fuel oil and its use on board a vessel, and these can be conveniently subdivided into, safety and pollution. The regulations fall into three categories, namely international, national, and those of the organization under which the vessel is classified.

The principal danger from marine fuel oil on board a vessel is that of fire, which may originate from the fuel itself, or may be exacerbated by the fuel in a fire that has already started. In order to minimize this risk, safety regulations have been developed to reduce these possibilities by restricting the flash point of the oil used. Also, arrangements have been evolved which prescribe the storage, distribution, and utilization of the fuel to ensure the safety of the ship and the people on board.

The main regulations are summarized below:

(1) The flash point of the fuel used in the main machinery spaces shall not be less than 60 °C. For fuel used external to the main machinery spaces in the case of an emergency, for example lifeboats, the flash point of the oil shall not be less than 43 °C. The flash point shall be determined by the closed cup method.

(2) As far as is practicable, pipes containing heated oil under pressure shall be readily observable. Also the machinery spaces in way of such parts of the fuel system shall be adequately illuminated.

(3) Ventilation under all normal conditions shall be sufficient to prevent accumulation of oil vapour.

(4) Fuel oil tanks, so far as is practicable, shall be part of the ship's structure and located outside the main machinery spaces. In general, the use of free-standing fuel oil tanks shall be avoided.

5 Fuel oil tanks shall be sited so that no spillage or leakage can cause a hazard by falling on heated surfaces. Similarly, drip trays shall be fitted around pumps, filters, and heaters to prevent the spraying of oil under pressure coming into contact with heated surfaces.

(6) Shut-off valves which can be operated from outside the machinery space shall be fitted to outlets of all fuel oil storage tanks.

(7) Safe and efficient means must be provided for measuring the amount of fuel in a fuel oil tank.

(8) Safe provision shall be made to prevent over-pressure in any oil fuel tank or any part of the oil fuel system.

(9) Oil fuel pipes, valves and fittings shall be made of an approved material.

Regulations alone do not, however, prevent casualties and damage to the ship, and are of no effect if simple precautions are neglected. Cleanliness is essential to safety, and almost without exception casualties and ship damage are a result of human error and improper practices.

In some ports and local geographical areas there are pollution regulations which apply to the emissions arising from the burning of marine fuel. These are with reference to sulphur, and in order to meet these regulations it is necessary for vessels under these jurisdictions to burn fuel which is sulphur-limited. In order to meet these regulations it has been necessary for vessels to have additional storage tanks on board in order to satisfy this requirement.

Pollution can also take place by the discharge of oil into the sea. Although marine fuel is purchased by the shipowner in order to be burnt, this objective may not always be achieved, and under certain circumstances there may be quantities of oily water sludge for disposal. So as to avoid pollution this residue must either be burnt on board or discharged ashore to reception facilities after separation of the included water. Discharge at sea is forbidden by international law, except under well defined conditions. These regulations include the following requirements:

(1) The ship must be proceeding *en route*.

(2) The instantaneous rate of discharge of oil content of the water must not exceed 60 litres per mile.

(3) The oil content of the discharged water must be less than 100 parts per million of the mixture.

(4) The discharge must be made as far as is practicable from land.

The current legislation only states the conditions and procedures, but does not specify in detail the equipment required. MARPOL 73 (1973 International Convention on Marine Pollution) gives detailed specifications and tests for separating and monitoring equipment. Unfortunately the major obstacle to the ratification of the 1973 convention is the lack of reception facilities in many ports throughout the world. Such facilities are expensive to install, and some countries are reluctant to provide them. If the necessary minimum number of countries sign the ratification document before reception facilities are provided on a world-wide basis, then ships will either have to be fitted with a means of burning this residue on board, or have fairly extensive tankage on board for the storage of sludge and similar oil-contaminated mixtures for eventual discharge ashore.

In addition to international legislation, within their territorial waters many countries have legislation on this subject. Since 1922, the United Kingdom has forbidden the discharge of any oil from bunkers (Oil in Navigable Waters Act).

LEGAL ASPECTS

The legal aspect is a complex subject because of the numerous legal systems under which bunkers may be supplied. Under most legal systems it is understood that a bunker contract is a 'contract for the sale of goods'. But the interpretation of such a contract, in the event of a dispute, depends on the jurisdiction under which the contract was made.

Under English law, the rights and liabilities which arise from the supply of bunkers are similar to those associated with any contract for the sale of goods. Apart from instances of fraud, the customer gets what he asks for—save that the doctrine *caveat emptor* (buyer beware) is tempered by the Sale of Goods Act 1979. This Act protects the customer as to the product's merchantable quality, fitness for purpose, and answerability to its description. In the case of a time charter, it is usually the charterer who agrees to provide and pay for the bunkers supplied to the ship for the duration of the charter. The supply may be arranged under a world-wide contract with an oil company or be made from the 'spot' market. The bunker agreement is between the time charterer and the oil supplier, not the shipowner. By stating in the charter party an agreed grade of fuel the sometimes tortuous legal issues surrounding 'bad' bunkers and charter parties could be significantly reduced. Under other jurisdictions different laws and codes are applicable, and the effect of each would require detailed study by legal experts. Similarly the meaning of any quality disclaimers included in a contract would require study, and may have different interpretations under various jurisdictions.

SHIPBOARD TREATMENT OF MARINE FUEL

Once a vessel has bunkered fuel, before the fuel is burnt in either a diesel engine or boiler, shipboard treatment of the fuel takes place. In the case of vessels burning a distillate the treatment will probably only consist of a filter, which may be of the coalescent type in order to trap any water that is present. For vessels burning residual fuels the shipboard treatment will be more extensive. The arrangements vary, and depend on whether the vessel is a steamship or motorship. For a steamship in addition to settling tanks, cold and hot filters would be installed in the system prior to the fuel being burnt in the boiler. In the case of a motorship, which accounts for over 95 per cent of the world's merchant fleet in terms of number of vessels, the shipboard treatment is more complex. In addition to settling tanks and filters, centrifuges are installed in the vast majority of such vessels for the shipboard cleaning of the fuel.

There are several types of centrifuge used for the shipboard cleaning of fuel, the first of which was introduced over fifty years ago, and is the solid bowl type. In this arrangement the extracted solids collect at the periphery of the bowl, and the machine has to be stopped for manual cleaning. Around 1950, total discharge self-cleaning models were introduced. These machines have ports around the periphery of the bowl which are normally sealed off by a

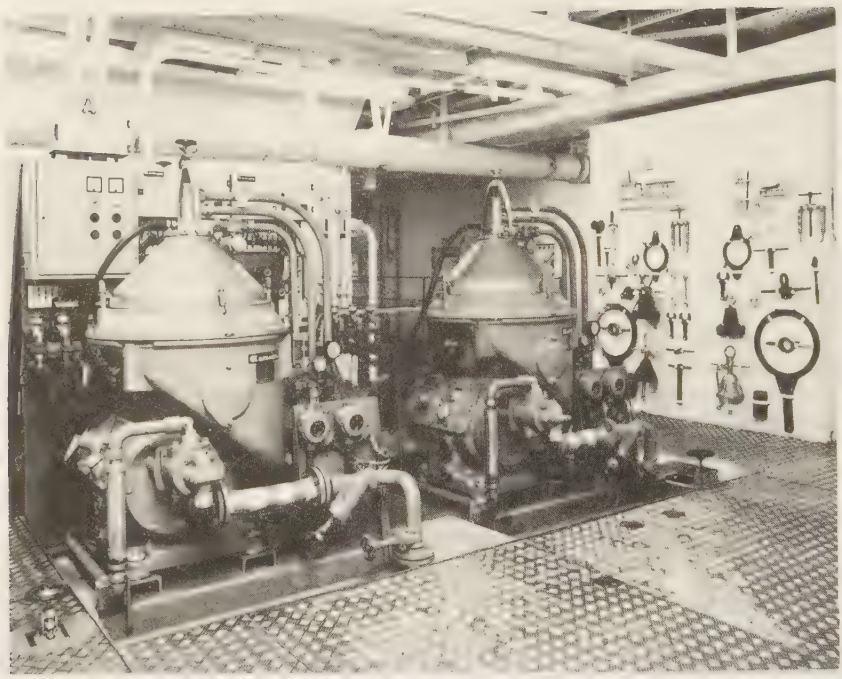

Fig. 5.

hydraulically-operated sliding bowl bottom. This can be lowered to expose the ports, and the entire bowl content can be discharged at selected intervals whilst the machine is running. The most modern type of machine is of the controlled partial discharge type. These machines also have a sliding bowl bottom, but the peripheral ports are exposed for a very short period, so that only the accumulated sludge and a measured quantity of water are discharged. With this type of machine the liquid feed remains on during the entire operating period. Part of a typical modern shipboard centrifuge system is shown in Fig. 5.

The separating ability of any centrifuge depends on the design and speed of the bowl, which develops approximately 5000–7000 times the force of gravity at full speed. In addition to this force, two other principles are used, namely thin strata distribution and that of the balanced column.

The bowl is fitted with 50–150 conical stainless steel intermediate discs, and the number is a function of the bowl size. These discs are separated by a series of caulks, fixed to the upper side of the disc, a distance of 0.5–0.6 mm, as shown in Fig. 6. On entering the bowl the untreated oil passes downwards as shown in Fig. 7. Then by centrifugal force the untreated oil is carried towards the periphery of the bowl and passes up through the disc pack, and the actual separation takes place in the channel formed between each two intermediate discs. The velocity of the oil is greatest at the centre and nearly zero at the disc surface. Each particle, solid or liquid, is acted upon by two forces. On the one hand, the particle is being forced upwards with the oil stream towards the centre, whilst on the other, centrifugal force is directing it to the periphery. It is

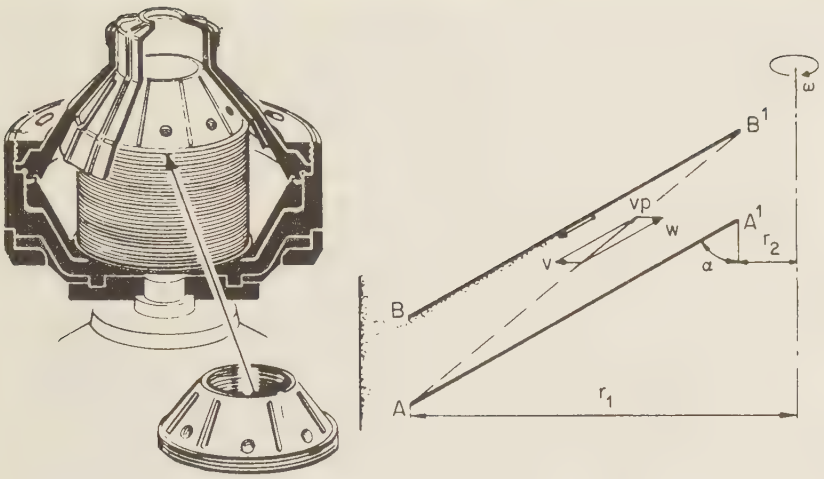

FIG. 6.

the resultant of these two forces which determines the path of the particle between the discs.

In order to be separated out, the particle must be deposited on the upper disc (B–B¹ in Fig. 6), that is at a radius $\geq r_2$. The particle is considered to have separated out on reaching the disc stack surface, and as the liquid velocity is negligible, the particle moves outwards by centrifugal force towards the periphery of the bowl. For the worse case, the particle starts from the most difficult position, namely A in Fig. 6, and moves along the dotted line as shown, so that it is barely separated out at point B¹. In this case all the larger particles will become separated out. Hence the smaller the particle the closer to point B it must enter the disc pack. Thus, maximum separating efficiency is a function of rotational speed ω, angle of the disc pack and the distance between the discs.

The liquid feed of untreated oil is usually a mixture of oil, solids, and water which the centrifuge separates out into three layers. During the running period a quantity of water remains in the bowl to form a complete seal around the

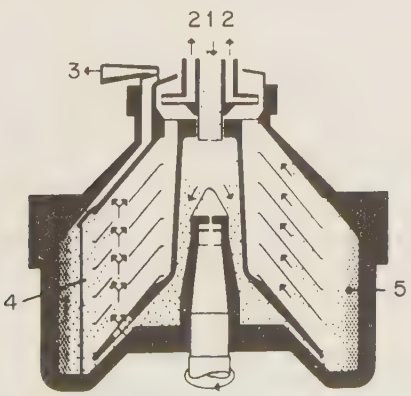

FIG. 7.

underside of the top disc and confines the oil within the outside diameter of the top disc. Hence a column of water balances a column of oil, using the balanced column principle. As marine fuel normally only contains a small quantity of water, it is necessary to prime the bowl each time it is run; otherwise all the oil will pass over to the water outlet side to waste. The cylindrical division between the oil and water is known as the interface, and the position of this interface is critical when the centrifuge is operated as a purifier.

In fact, the centrifuge can be used for two types of operation, which are purification and clarification. Used as a purifier the centrifuge for marine fuel is separating two liquids, namely water from oil. The heavier liquid is forced towards the bowl periphery, and the lighter towards the bowl centre. Each leaves the centrifuge through its own outlet, and any contained solids will accumulate at the periphery. When used as a clarifier the centrifuge has only one outlet for the treated liquid, and the extracted solids are accumulated at the periphery. When a centrifuge is operated as a clarifier small amounts of water can be accommodated which will build up in the bowl. Figure 7 shows the two arrangements, with purification on the left and clarification on the right.

The position of the interface is critical for effective purification, and is altered by the variation of the heavy phase (water) outlet diameter. Reference should be made to the manufacturer's instruction manual for the selection of the correct diameter. For this purpose a number of discs known as gravity discs are supplied with each machine. The size of the disc fitted depends on the density of the untreated oil. If the gravity disc is too small the separating efficiency will be reduced as the interface will be formed within the disc pack. If the diameter within the gravity disc is too large, the interface will form at a diameter greater than that of the top disc, and the treated oil will pass to waste through the water outlet. In addition to the density ratio between the oil and water, there are other factors which can influence the position of the interface. These are viscosity, flow rate, and variation in density. A decrease in viscosity, due to an increase in temperature, a decrease in flow rate, or a decrease in density will result in the interface moving into the disc pack, reducing efficiency. Conversely, an increase in viscosity due to a decrease in temperature, an increase in flow rate, or an increase in density, will move the interface towards the periphery, ultimately resulting in a loss of the liquid seal. The optimum position of the interface is between the edge of the disc stack and the outer diameter of the top disc.

So as to reduce the frequency of changing gravity discs as a result of changes in density from different bunkerings, some modern centrifuges are fitted with a manually-operated interface control device. This device is available for centrifuges with a paring disc discharge pump for the treated oil, and consists of a pressure-balanced pneumatic valve, fitted into the discharge line. By applying a counter pressure to the discharge line the interface can be moved outside the disc stack without changing the gravity disc. This feature, however, does not replace the requirement for effective control of throughput and temperature.

ADDITIVES

Under certain circumstances, following careful assessment of the plant, operating conditions and the fuel quality, the use of additives in the marine fuel

can be advantageous to the shipowner. In overall terms the introduction of additives must be cost effective, otherwise the vessel's operating cost is increased unnecessarily. There are two distinct categories of additives, namely those which assist in reducing potential problems in pre-combustion and those which react during the post-combustion phase.

The pre-combustion phase covers the period from receipt of the fuel onboard, up to the time that it is atomized in a burner or an injector. Thus the period covers storage on board and the shipboard treatment of the fuel. An effective additive for this phase should be able to make a positive contribution to the following aspects:

1. Dispersion of possible sludge in the fuel tanks.
2. Promotion of the separation of any dispersed water within the fuel.
3. Prevention of potential polymerization and sludge formation.
4. Prevention of corrosion within the fuel lines and tanks.

Such an additive would be based on aromatic solvent carriers, dispersants, anti-corrosion agents, anti-oxidants, emulsion breakers, and have alkaline properties. The solvents present would break up sludge and re-dissolve some of the oxidation and polymerization products formed as a result of any sludge. The interfacial tensions which occur between the sediment and oil are lowered, so reducing the tendency for particles to coalesce. The effect of the emulsion breakers is to assist in the release of water from the oil, whilst the anti-polymerization agent reacts with unsaturated chemical double bonds, preventing the formation of long hydrogen/carbon chains which would precipitate as sludge, and is also absorbed on metal surfaces, tending to create a film which prevents corrosion of surfaces.

During the post-combustion phase the potential areas of concern depend upon the category of plant installed. In the case of a steamship, there is the possibility of corrosion of the superheater tubes, slag build-up on both the superheater and steam-generating tubes, low-temperature corrosion, and carbon deposition in the regenerative parts of the boiler, namely the economizer and air heater. For diesel engines the potential areas of concern are corrosion of exhaust valves, turbocharger fouling, carbon deposition, and low-temperature corrosion.

In order to reduce the problems that may occur in the post-combustion phase an additive which has the effect of an ash modifier may under certain circumstances be beneficial. As already discussed the ash is related to the inorganic material in the fuel oil, and the compounds formed due to this material, when burnt with the oil are complex. The actual type of compound formed and its properties depend upon the operating conditions, and are also influenced by the sulphur gases present and carbon. Slagging and high-temperature corrosion occur when molten ash adheres to the metal surfaces, and there is a reduction in heat transfer. Hence, the ash modifier should have the ability to increase the melting point temperature and make the ash more friable. By increasing the melting point, the temperature may reach a point when the ash is not in a molten form and will not be corrosive. In being more friable the ash is less likely to stick to metal surfaces and affect heat transfer.

Numerous ash-modifying chemicals are available; these include compounds based on aluminium, barium, calcium, magnesium, and silicon. These

different compounds affect the melting process in different ways, and the physical nature of the conditioned ash also varies depending on which compound is used. Aluminium tends to produce light but voluminous compounds, whilst those based on barium and calcium tend to form hard insoluble deposits. Magnesium-based ash-modifiers give rise to very voluminous deposits. Silicon-based compounds for this application produce dry friable non-adhesive deposits. Situations can arise when the effect of the ash-modifier, by incorrect application, can cause further problems in the downstream post-combustion phase.

Some additives are termed 'combustion catalysts' which must be regarded as a convenient name, as it is unlikely that the chemicals used remain unchanged at the end of the reaction; they do, however, influence the reaction, and are present in relatively small quantities. The function of the 'combustion catalyst' is to cause the carbon to be more extensively burnt, and inhibit the formation of carbon precursors. The 'combustion catalyst' can be a single metal or a metal combination, usually involving transition elements. The metals commonly used are magnesium or iron, or combinations of these two. Dosage of 'combustion catalysts' is not as critical as with ash-modifiers, and to be fully effective the supplier's instructions should be most carefully followed.

ALTERNATIVE FUELS

The first fifty years of this century witnessed the evolution to effective total use of marine fuel oil for merchant ships. How long this situation will last depends upon the future availability and price of marine fuel oil. An alternative energy source would need to have world-wide availability and a stable price. Further, it would need to be plentiful and not concentrated in a specific country or economic unit where it may become subject to excessive political control. Also ease of production, distribution, and storage are all important requirements.

Nuclear power has been considered for over twenty years as a possible source of energy to take the place of oil for merchant ships. Although there are over three hundred nuclear-powered military ships, only five nuclear-powered merchant ships have so far been built, of which only two are currently in service. These are two Soviet ice-breakers. Various studies have shown that for high-powered merchant ships, nuclear power, despite the high capital cost, could be competitive with oil in economic terms. There are, however, several basic reasons why the nuclear-powered merchant ship is unlikely to find universal acceptance in the foreseeable future. The public concern over the accidental release of radio-activity has not been reduced by the upward trend in casualty statistics, and the problem of insurance against damage or loss appears to be an international problem which can only be resolved at inter-governmental level. Even with resolution of the insurance problem, the development of land-based ship support establishments in existing port areas could result in extensive opposition from the local population, and requires new developments in relatively remote 'greenfield' sites. Nuclear energy is surrounded by emotive issues in many industrialized countries which seem no closer to resolution with the passing of time. Nuclear power remains a question mark in the assessment of future world-wide energy supplies, and its earlier slow gain in development

may well have a significant effect on the future price, availability, and quality of marine fuel oil.

Methanol has certain attractions as a marine fuel, because it is a liquid at ambient temperature and pressure. Its specific energy and density are both substantially less than those of oil, and hence substantial extra bunker volume would be required. It may be produced from coal or natural gas, or could be synthesized from limestone or air using nuclear-generated electricity. If such a fuel was adopted, attention would have to be given to ensure high-level concentrations did not occur, because methanol is moderately toxic. Normal exposure to low concentrations of methanol fumes is not damaging to health.

Hydrogen has a high heat content per unit weight relative to oil, but in a gaseous state has a high specific volume. If stored in a refrigerated state and volume is not at a premium, hydrogen provides a potential source of energy. However, the production of hydrogen from non-fossil sources requires nuclear heat or electricity, so as with methanol there is a large energy component in its production, and its use will be costly where lower cost alternatives are suitable and available. Methane as an alternative energy source has been discounted, since its availability is linked with that of oil. As ammonia and hydrazine are both highly toxic, they have also been discounted. Wind was used for centuries as a source of energy to transit the oceans of the world, and it is possible that for certain specific trades, there could be a revival of the auxiliary sailing ship in the longer term.

Coal is likely to form the most suitable alternative to oil in the provision of energy for the propulsion of ships in the future. The world's reserves of coal are vast, and in energy terms dwarf those of oil. Coals such as anthracite and bituminous and semi-bituminous coal are suitable for world-wide ship operation. The use of these coals would double the bunker volume required on board ship relative to marine fuel oil, besides requiring complex and space-consuming coal- and ash-handling plants. With present technology coal is suitable for plants utilizing a continuous combustion system, such as steam turbine plants.

Pulverized coal is one possibility, and was used nearly fifty years ago in s.s. *Musician*. In a future plant, pulverizing mills would be needed on board to reduce the coal to a finely-divided state from the raw coal that would be bunkered.

Historically the handling of coal, both in bunkering and internal transfer to the boilers on board ship, was a labour intensive and dirty operation. Today handling of solid coal in a socially acceptable manner may be achieved mechanically or pneumatically.

Liquefaction and gasification of coal have been technically possible for some time, and new technology is sought only for economic reasons. It is considered by some that liquid fuels from coal could be economic as measured against available alternatives by the end of the century, but as such liquid fuels would be high-grade products, they are unlikely to be accepted in the marine fuel market, so long as lower-grade and hence less expensive products were available. Similarly, hydrogenation of coal to produce synthetic oil is not considered a serious contender as a means of producing a fuel for a service in which an essentially low-grade fuel will suffice. Reduction to a slurry would seem to be more suitable where coal is to be stored and utilized in a fluid form.

Coal/water and coal/oil slurries are both products which will reduce the transportation and storage difficulties experienced with coal in solid form. Slurries have potential for practical application to marine machinery. The limit of coal that can be carried in a residual oil is about 45 per cent by weight, and exists because of the compaction of coal. Use of a coal/oil mixture could well result in a fuel which could be considered fully interchangeable with marine fuel oil, so far as a steamship is concerned. This could, therefore, form an initial transitional step from an oil-fired fleet to a coal-fired fleet, as the availability of oil decreases and substitution becomes essential. Some marine diesel engine manufacturers see a coal/oil mixture (COM) as a possible future fuel. However, in present generation marine diesel engines, the use of such a fuel would cause a significant increase in maintenance and a reduction in ship availability, and substantial engine development would be needed. Introduction of a commercial coal/oil fuel would require the development of a new supply infrastructure in the marine market, and is unlikely with the present make-up of the world merchant fleet.

COM would not be attractive in the marine fuel market-place until the delivered price per unit energy is at least 30 per cent below that of the price of marine fuel oil. This is the order of cost differential necessary to offset the economic advantage of operating diesel engines as opposed to steam plant of lower thermal efficiency, and would require coal to be available at less than one-tenth the cost of residual fuel oil. The implied low cost of coal, and the high cost of oil precludes its adoption other than as a bridging fuel, and lower cost alternatives must be utilized as the main long-term energy source for marine use.

Petroleum coke/oil is an alternative bridging fuel even though the constituents are all derived from crude oil. Such a fuel is an 'opportunity' fuel, depending on the value given to low-grade coke. As already mentioned the present barrel lightening programme is orientated towards the visbreaking of residue, and the limit to which it can be applied depends on fuel oil stability. The production of petroleum coke is not at present the preferred barrel lightening route, because there are insufficient markets for low-grade coke.

Petroleum coke/oil may have limited potential as a shipboard fuel. The abrasiveness of the combustion products would be significantly less than those from a COM fuel, and although the abrasive particles of the petroleum coke would create wear problems in existing marine diesel engine fuel injection systems, this is not considered to be an insurmountable design problem. Ultimately, the attractiveness would depend upon the price relative to fuel oil.

It is considered that the diesel engine will continue to gain an increasing share of the marine propulsion market for the foreseeable future. This continuing dominance will exist as long as a suitable liquid fuel oil is made available in the requisite quantity so that there is no extreme price escalation resulting from a gross shortfall in supply. In some trades where circumstances permit, coal will be adopted on a limited basis. However, in such circumstances the low cost of coal will outweigh the less efficient energy conversion cycle of the steam plant. The widespread introduction of such ships is expected to be very slow, and the next two decades at least will see liquid-oil-fuelled diesel engines as the predominant prime movers in new vessels.

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25

Petroleum Hydrocarbon Solvents

By J. BRAMLEY and L. TURNER

INTRODUCTION

Hydrocarbon solvents are volatile fractions derived either directly or indirectly from petroleum. The distillation range and composition are selected by the manufacturer to suit the various end-use requirements.

These solvents are used in a wide range of products and industrial processes; they may comprise part of a finished product as in the manufacture of paint, printing inks, polishes, adhesives, etc.; they may be used in extraction processes within a plant such as the extraction of vegetable oils from oil seeds, minerals, pharmaceuticals; or they may be used simply for clean-up and maintenance operations. World demand in 1980, excluding usage in the centrally planned economies of Eastern Europe, is estimated to be in excess of six million tons. This estimate excludes demand for benzene, toluene, xylene, and cyclohexane which find major uses as chemical intermediates. The important grades of hydrocarbon solvents are clear, water-white liquids which are immiscible with water, but are completely miscible with other commonly used organic solvents. Their ability to dissolve substances depends on the relative proportions of aromatics, naphthenes, and paraffins present. They are good solvents for many resins used in surface coating preparations, and for oils, fats, greases, waxes, bitumen, etc.

COMPOSITION

Although a few pure hydrocarbons are available in bulk commercial quantities for use as solvents, e.g. toluene, cyclohexane, almost all hydrocarbons solvents are mixtures of chemically distinct hydrocarbon molecules. The composition of a particular solvent is usually quoted in terms of the types of hydrocarbons present, i.e. paraffins, naphthenes (cycloparaffins), aromatics, and olefins. The proportion of these groups of hydrocarbon types has an effect on physical properties such as solvent power, viscosity, density, and odour.

Small amounts of non-hydrocarbon compounds such as sulphur and oxygenated materials can be present, but are usually removed to very low levels during the manufacturing process. The olefin content, characterized by the bromine index, is usually low. For certain very critical end-uses grades are available which are virtually free of any unsaturation.

CLASSIFICATION

As nearly all commercially available hydrocarbon solvents are derived from the fractionation of a petroleum stream, distillation range is the main classification. For end-uses where the solvent evaporates after doing its job, e.g. in paint, solvents are often grouped as slow, medium, or fast evaporating.

Increasingly solvent power and odour are becoming critical properties in certain sectors, and the classification of hydrocarbons according to their content of aromatics is common. Usually three categories are used: high, normal, low (de-aromatized). Some examples of products in these various classes are given below.

SBPs (Special Boiling Point Spirits)

These are essentially aliphatic solvents with both narrow and wide boiling grades within the temperature range 45–160°C. Table I shows some standard grades which are available in the UK.

TABLE I
Special Boiling Point Spirits

Grade	Density at 15°C (kg/l)	Distillation range IBP–DP (°C)	Aromatic content (% m/m)	Flash point (°C)	KB value
SBP 65/70	0.675	66–70	<0.1	< −30	30
SBP 1	0.677	46–113	<0.1	< −30	30
SBP 2	0.697	74–94	<0.1	< −30	33
SBP 3	0.720	100–121	<0.1	−2	30
SBP 4	0.689	48–148	2	< −30	30
SBP 5	0.713	90–103	<0.1	−12	33
SBP 6	0.767	140–163	17	30	36

Isoparaffinic Solvents

Rather than being refined and treated petroleum fractions, isoparaffinic solvents are manufactured from lower molecular weight hydrocarbons by a process called alkylation. These solvents consist essentially of isoparaffins with negligible amounts of other hydrocarbon types. They are characterized by a lower solvent power than conventional grades, but have the marked advantage that for all practical purposes they can be considered as odourless.

Aromatics

A full range of aromatics solvents are available; the faster evaporating types are essentially toluene and xylene (benzene is no longer recommended for general solvent use). For slower evaporating solvents the chemical composition is complex and the various products are characterized by the more important physical properties.

White Spirits

These solvents boil within the range 150–220°C, but rarely within less than 20°C. In the UK the most common grades are the normal (100°F flash point) and the high flash (115°F) white spirits. Obviously the high flash grade has a somewhat slower evaporation rate and higher final boiling point. White spirits

are not de-aromatized and will have aromatic contents depending on the crude oil source; this is usually selected to give approximately 17% vol aromatics.

De-aromatized Solvents

Solvents are available now which have been de-aromatized to various extents. These solvents have much lower odour than conventional regular grades. The process used to manufacture these grades is usually based on hydrogenation which not only converts aromatics into naphthenes, but also gives products of very low reactive impurity levels. A comparison of some physical properties of products boiling in the white spirit boiling range can be seen in Table II.

TABLE II
De-aromatized Solvents

	Density at 15°C (kg/l)	Distillation range IBP-DP (°C)	Aromatic content (% m/m)	Flash point (°C)	KB value
Shellsol D40	0.762	162–197	<0.5	40	31
Shellsol D60	0.783	185–219	<0.5	61	30
Shellsol D70	0.790	194–251	<0.5	72	29

NOMENCLATURE

There is no universally accepted nomenclature used for hydrocarbon solvents. Some of the systems and synonyms in use are as follows:

SBP—Special boiling point spirit.
Represents a range of products often characterized by a number, e.g. SBP 1, SBP 2, etc.
Petroleum Spirits is also used for SBPs.
Names such as Hexane, Isohexane, Heptane, etc. for SBPs (paraffins) which may consist mainly (but not entirely) of the named hydrocarbon.
Petroleum ether for SBPs boiling below 100°C, a very undesirable name for a hydrocarbon.
Mineral Turpentine/Mineral Spirits/Stoddard Solvent—for white spirit.
Kerosines (Kerosols)—for solvents boiling between 160–300°C.
Ink solvents—solvents with narrow boiling range between 220–310°C.
BTX—benzene, toluene, and xylenes.

Most manufacturers group their solvents according to composition, i.e. low aromatic, high aromatic, isoparaffinic, etc., and assign a number or letter to each fraction in the particular group according to boiling range.

MANUFACTURE

In general, hydrocarbon solvents are manufactured in oil refineries. Originally fractions were obtained by drawing off suitable streams from crude oil distilling

columns, followed by various treatments to reduce odorous and/or corrosive impurities.

Gradually quality requirements have become more critical and grades more diverse so that other refinery streams are used as feedstock (e.g. platformate and alkylation streams), available from other refinery processes. Also, blending of product streams and conversion and/or separation of constituents (e.g. by extraction, hydrogenation) have been introduced. Hydrocarbon solvent feedstocks are often pretreated prior to distillation to give products of the desired properties.

Manufacture of hydrocarbon solvents generally involves three separate stages:

1. Distillation, which gives the product its specific position in the volatility scale.
2. Chemical conversion and/or separation; this gives the hydrocarbon a specific composition according to molecular type and affects largely solvent power.
3. Treatment to remove various minor impurities from the products.

A fourth step is sometimes used for very specific requirements, namely, blending. These 'tailor made' products are often blends of aliphatic fractions with pure aromatics to give the required solvent power.

The three main steps are considered in more detail in the following paragraphs.

Distillation

It is sometimes possible to obtain hydrocarbon solvents with the correct boiling range from a single-step main refinery unit. However, most solvents are manufactured in purpose-designed distillation facilities from mainly hydrotreated/hydrodesulphurized feedstocks. Owing to increased demand for very narrow boiling range products—often about 5 °C—solvent distillation columns with more than 70 trays and reflux ratios of 3:1 are normal today.

For high boiling solvents, for example ink solvents, distillation at reduced pressure is normally applied to avoid high distillation and reboiler temperatures which could have an adverse effect on product quality.

De-aromatization

For many applications, solvents obtained by distillation and hence having the hydrocarbon composition typical of that of the feedstock from which they have been made, are acceptable, and thus no chemical conversion or separation of hydrocarbons is required.

Crude oils contain varying amounts of aromatic hydrocarbons depending on their origin, and hence the fractions distilled from a crude oil will also contain these aromatics. If SBPs were manufactured by straight distillation they would contain the aromatics benzene, toluene, and xylenes (boiling points 81 °C, 110 °C, and 136–144 °C), usually in small amounts of around 5 per cent down to less than 0.5 per cent of benzene, but gradually rising up to 15 per cent in the

case of xylenes. Similarly, straight-run white spirits contain about 15–20 per cent of mainly C_9, C_{10}, and C_{11} aromatic hydrocarbons.

For both performance and toxicological reasons there is an increasing demand for solvents that are essentially benzene-free and have very low aromatic contents. Examples of applications where solvents with very low benzene contents are required are oil seed extraction, printing inks, adhesives, and for performance reasons in polyolefin manufacture. The removal of aromatics from a solvent fraction gives a marked improvement to the solvent odour; for this reason de-aromatized solvents in the 150–250°C distillation range are gaining popularity.

Several methods are available for de-aromatization; however, only two are of large commercial importance, i.e. hydrogenation and solvent extraction. In terms of product quality and product performance there are differences between de-aromatized solvents manufactured by the two routes. Hydrogenation not only converts aromatics to naphthenes, but also converts unsaturated impurities to inert paraffins. Extraction processes can produce solvents with very low aromatic contents, but the unsaturates remain unchanged. Also the hydrogenation process results in products where the loss in solvent power due to aromatic removal is largely compensated by the increased naphthenic content.

(*a*) *Hydrogenation*

Conversion of aromatics to naphthenes is achieved by catalytic hydrogenation. This process of de-aromatization is becoming more usual in locations where hydrogen is already available. The process uses a hydrogenation catalyst which is supported on a carrier. Many types of catalyst have been used, e.g. platinum, palladium on silica or alumina, nickel; these require low-sulphur feedstocks which are usually prepared by hydrotreatment. Other catalyst systems have been developed for direct hydrogenation of high-sulphur feedstocks, e.g. nickel/tungsten catalyst. The pressures and temperatures used in the catalyst column are dependent on the type of catalyst, throughput of feedstock and quality requirements; some typical ranges would be: pressure 50–100 bars, temperature 200–350°C.

A typical flow scheme for a hydrogenation unit is given in Fig. 1.

(*b*) *Solvent extraction*

For several decades solvent extraction of aromatics from high boiling crude oil fractions, for example, kerosine, lubricating oils, etc., has been practised in oil refining to produce fuels and lubricants of lower aromatic content and hence of improved quality. The extracted aromatics are suitable raw materials for the manufacture of aromatic solvents and aromatic process oils. Extraction of aromatics from kerosine is usually undertaken by means of the process developed by Edeleanu, which uses liquid sulphur dioxide as extraction solvent. Rigorous extraction of the kerosine results in almost aromatic-free raffinates which are used for the production of odourless kerosine (more correctly, low-odour kerosine). A range of highly aromatic white spirits and kerosine solvents may be manufactured from the kerosine extracts.

If more or less pure aromatic extracts are required, sulphur dioxide may not

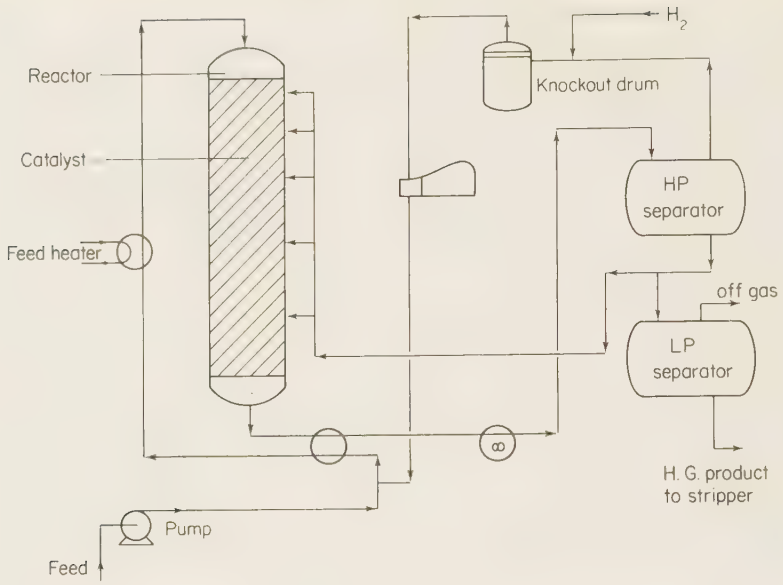


Fig. 1. Hydrogenation unit.

be used alone, and a second solvent, for example a light or heavy paraffin, would be needed. Such a two-solvent system would be complex and expensive.

More recently developed extraction processes for the separation of aromatics and non-aromatics use solvents with much higher boiling points than that of sulphur dioxide. Such processes are very versatile in that raffinates with very low, as well as extracts with very high aromatics contents can be made.

Of the processes available, the Shell sulfolane extraction process is one of the more widely used, especially for the extraction of pure aromatics from hydrocarbon mixtures and/or the production of low-aromatic solvents.

In this process (Fig. 2) the feedstock and the heavy solvent sulfolane are fed counter-currently to an extractor, for example a rotating disc contactor (RDC), At a temperature of approximately 100°C, the solvent dissolves practically all of the aromatics from the feed, thus leaving a virtually aromatic-free raffinate. However, the solvent dissolves some of the lighter non-aromatics as well as the aromatics. The fat solvent from the bottom of the extractor is fed to the extraction distillation column, where the non-aromatics are rather easily stripped off from the solvent/aromatics mixture. The non-aromatics top product is fed back to the extractor bottom and re-cycled, thus serving as backwash to reduce the dissolving of the heavier non-aromatics, which are more difficult to separate from the extract phase. From the bottom of the extractive stripper, sulfolane containing pure aromatics is fed to a solvent recovery column where the aromatics are taken overhead. To limit solvent losses to a minimum, the raffinate, which contains a few percent of sulfolane, is washed with water. The water is then used to provide stripping steam in a recovery column and goes overhead with the extract, settles out, and is used again for the raffinate wash. Both the raffinate and the extract may be used as such or after splitting into the required cuts by fractionation.

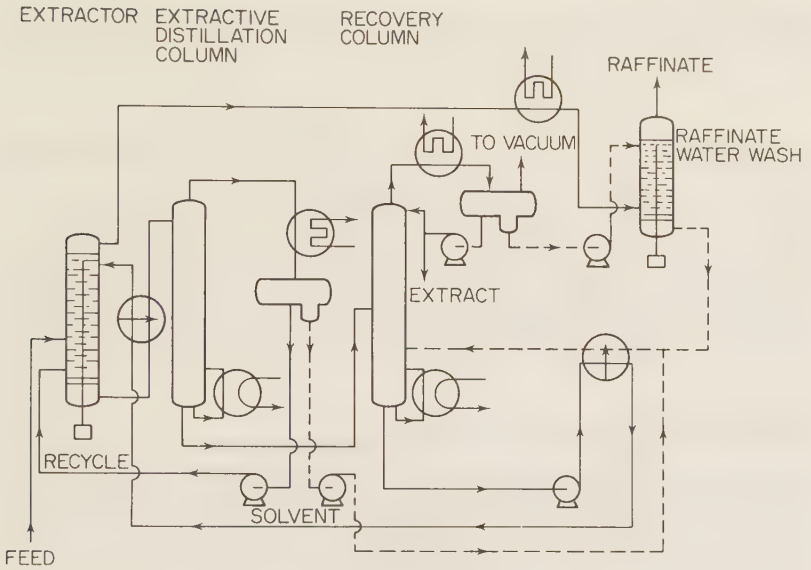


FIG. 2. Sulfolane extraction unit.

(*c*) *Other procedures*

Several other procedures have been used for de-aromatization, but they are often associated with disposal problems. An example is oleum treatment. By sulphonating the aromatics with oleum (sulphuric acid + SO_3) the aromatic can be separated in the oleum phase. Obviously the hydrocarbon phase needs washing and neutralizing with caustic soda before further processing. This process has lost popularity, mainly due to the problems of disposing of the waste caustic soda and acid. It also results in a higher hydrocarbon loss than the conventional hydrogenation or solvent extraction techniques.

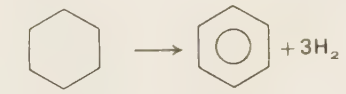
This technique is still used in the laboratory separation of mixed solvents prior to analysis.

The use of selective absorbents, such as silica gel, alumina, and activated carbon, is not attractive for large-scale commercial production. They are mainly used to remove trace active impurities, as drying agents, and to remove coloured or odorous materials.

Aromatic Solvent Manufacture

The close links between oil refining and hydrocarbon solvents production are well illustrated in the case of aromatics (BTX) manufacture. Catalytic reforming of light crude oil distillates has been carried out for over thirty years as a method of producing high-octane gasoline components. Essentially this process converts naphthenes present in the light distillate feedstock into aromatics, and is now the basis for much of the manufacture of benzene,

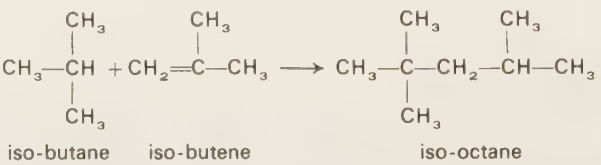
toluene, and xylenes. The process is also a very important source of hydrogen, and may be expressed simply as:



The heavier fractions from the reformer form the basis of a range of pure aromatic solvents boiling over 160°C. This heavy fraction is generally separated into three commercial solvents which have the best solvent power of this distillation range and are extensively used in stoving paint formulations.

Isoparaffinic Solvent Manufacture

Isoparaffinic solvents are synthesized by a process called alkylation. This process reacts low-boiling isoparaffins, e.g. iso-butane, with low-boiling olefins, e.g. iso-butene, to give isoparaffins of greater molecular weight. The reaction, in a simplified form, is shown in the following equation:



The fraction distilling in the gasoline range is usually taken up into fuel outlets, for example, aviation gasoline. The fraction boiling above 100°C may be distilled to give a range of solvents which are practically odourless. This property results from their high isoparaffin content (greater than 90 per cent). These solvents have a somewhat low solvent power which restricts their use, but when a no-odour product is required, e.g. in photocopying, household products, and odourless paints, etc., these solvents are the best choice.

Normal-paraffinic Solvents Manufacture

Commercial molecular sieve adsorption processes are now available which permit the manufacture of n-paraffins, not only for use as chemical intermediates (for example, for conversion to detergents), but also for use as hydrocarbon solvents. An example of such a process is Union Carbide's 'Isosiv' process.

This is mainly an efficient means for the recovery of 95 per cent pure normal paraffins from branched-chain and cyclic hydrocarbons by molecular sieve absorbents. Straight-chain hydrocarbons, having a diameter of less than 5 Å may enter the 5 Å mol sieve, while branched and cyclic hydrocarbons may not. Continued operation of this vapour phase process is achieved by the utilization of two fixed adsorption beds on a pressure swing cycle. The use of rather clean, i.e. hydrotreated, feedstock is recommended.

The removal of normal paraffins from crude oil distillates in the refinery usually enhances the value of the distillates as raw materials for fuels and lubricants.

Cycloparaffinic Solvents Manufacture

Apart from the manufacture of cyclohexane from benzene by catalytic hydrogenation, the manufacture of predominantly cycloparaffins is of minor importance for solvent end-uses.

Solvents of increased cycloparaffin content are, clearly, produced when aromatics are converted in the hydrogenation process, but to produce solvents with very high naphthenic contents specially selected feedstock streams are required.

Removal of Trace Impurities (Treating)

As is the case for many other oil products, a treating process is often required to produce marketable solvents, particularly since appearance, odour, and chemical stability are of the utmost importance. Solvents are often used in conjunction with chemically reactive substances, and they may also come into contact with equipment made in part from corrodible materials, for example copper.

Some hydrocarbon solvents are made from intermediate streams from which many unwanted impurities will already have been removed, for example, by hydrotreating. In such cases, chemical treatment for the removal of trace contaminants may no longer be necessary. Nevertheless, depending on the feedstock source and on other conditions in a particular refinery, specific treating of solvents by some of the under-mentioned methods may still be needed.

Hypochlorite Treating

With this process, it is possible to convert mercaptans to less obnoxious compounds, to extract part of the sulphur- or oxygen-containing compounds, and to provide an oxidative clean-up of the fraction handled. A drawback is that chlorinated hydrocarbons are formed, the removal of which may pose many problems.

Caustic Treating

It is possible to remove acidic contaminants such as hydrogen sulphide, carboxylic acids, and to a certain extent phenolics, and mercaptans with a caustic soda solution.

Acid Treating

Sulphuric acid, which in addition to having acid catalytic, oxidative, and solvent properties, may be used for the conversion and/or removal of various types of contaminants that may be present. It also reduces the total sulphur

content. However, as for oleum treatment, the disposal of the resulting acid sludge and of the neutralizing chemicals creates problems, and hydrocarbon losses may be considerable.

Hydrotreating

For general information on this process the reader is referred to Chapter 16. Hydrogenation of aromatics does not occur, so if this is required one of the special processes described earlier has to be used. Hydrotreated products possess a typical odour which may not be acceptable to the market, in which case a finishing step such as clay treatment is required.

Clay/Activated Carbon Treating

Sometimes hydrocarbons are treated by percolating through a bed of clay or activated carbon to improve certain quality aspects of the product. These treatments can improve acid wash colour and remove undesirable trace impurities which have an adverse effect on the odour of the product.

Solvent Blending

With the advent of the concept of tailoring to meet specific customer requirements, blending of components becomes of increasing importance in the production of hydrocarbon solvents. Blending may be carried out in order to achieve the particular evaporation characteristics required by a customer, in which case a solvent of the required volatility may be obtained from a small number of narrow-cut fractions, sometimes called building blocks. On the other hand, it may be desired to provide a solvent of specific solvent power, and then blending will involve two products of approximately the same boiling range, one of which is low in aromatics, the other a high-aromatic solvent or a pure aromatic. Ideally, a tailoring system should cater for both requirements simultaneously.

PROPERTIES

When hydrocarbon solvents are produced, care is taken to ensure as far as possible that their various properties are maintained at a consistent level. Manufacturing limits are set to allow for the changes that may occasionally occur in these properties when, for example, unavoidable feedstock changes intervene.

However, apart from isolated instances, for example British Standard 245 covering White Spirit for Paints, and the American ASTM standard D-484 for Mineral Spirits (Stoddard solvent), standard sales specifications for hydrocarbon solvents are few, and products are usually sold against typical properties.

The handful of solvents which consist essentially of only one hydrocarbon or its isomers, i.e. benzene, toluene, and xylenes, form an exception in that they are usually sold to standard specifications, for example, Nitration Grade toluene.

The properties which follow are often of importance in defining a hydrocarbon solvent, and in determining its usefulness as a solvent for a given purpose. Table III shows a selection of commonly sold hydrocarbon solvents with their main typical properties.

Several properties are important in the selection of a solvent in a particular end-use, since they have an effect on performance. The commonly considered properties are:

(*a*) *Evaporation rate*

The evaporation rate or 'volatility' of a hydrocarbon solvent is the most important characteristic in surface coating end-uses. The evaporation rate affects the drying rate, so solvent choice very much depends on the applicational conditions. The evaporation of a solvent from an applied film should be sufficiently fast to give a short drying time, to minimize dust collection and to allow early handling of the coated products. It should, at the same time, be slow enough to allow the development of a good film. The sharpness of distillation will have a marked effect on some end-uses, particularly the presence of a high boiling 'tail'.

Evaporation rates are measured using an automatic evaporometer (ASTM D3539) which gives a plot of weight loss against time under standard conditions.

An almost universally adopted procedure is to define a 'standard' solvent and quote the evaporation rates of other solvents relative to it. A widely used standard is n-butyl acetate, and this is assigned a standard evaporation rate of 1.0.

Some relative evaporation rates of hydrocarbon solvents are listed in Table IV.

(*b*) *Solvent power*

Solvent power is essentially a function of the relationship between solvent and solute, and is a term which is used rather loosely. It is sometimes used synonymously with solvency to cover not only the ability of a solvent to dissolve a resin, but its ability to reduce or to cut the viscosity of a resin solution. Thus, 'cutting power' is often used in the paint field and in similar industries, particularly where the viscosity of the final product is important. 'Solvent power' is, perhaps, more often used in the latter sense, so that 'solvency' tends to be confined more to the ability to dissolve.

An indication of solvent power may be obtained in a variety of ways: Kauri-butanol value, aniline point, dilution limit, and solubility parameters, etc. The Kauri-butanol value and aniline point are the ones most commonly used in the industry. The composition of a hydrocarbon solvent fraction also gives an indication of solvent power. As a rough guide for most polymers and resins, solvent power increases in the order:

$$\text{isoparaffins} < \text{n-paraffins} < \text{naphthenes} < \text{aromatics}$$

(i) *Aniline point.* Aniline is a poor solvent for aliphatic hydrocarbons and an excellent one for aromatics. This property is used in the aniline point test

TABLE III

Typical Properties of some Hydrocarbon Solvents

Property	Unit	Hexane SBP 65/70	SBP 2	SBP 3	SBP 5	White spirit
Distillation range	°C	66 70	74 94	100 121	90 103	153 197
Density at 15°C	kg/l	0.675	0.697	0.720	0.713	0.773
Flash point	°C	< −30	< −30	−2	−12	41
KB value		30	33	30	33	37
Aniline point	°C	65	61	63	62	55
Colour	Saybolt	+30	+30	+30	+30	+30
Evaporation rate (nBuAc = 1)		7.5	5.8	2.7	3.9	0.19
Viscosity at 25°C	mPas	0.31	0.38	0.48	0.44	0.85
Bromine index	mg Br/100 g	< 10	20	20	100	—
Aromatics	% m/m	< 0.1	< 0.1	< 0.1	< 0.1	17*

Property	Unit	Shellsol D40	Shellsol T	Shellsol A	Shellsol AB	Shellsol R	Odourless kerosine	Toluene	Xylene
Distillation range	°C	162 197	182–212	166 185	186–216	200–268	190–260	110.4 110.8	138.7–142.3
Density at 15°C	kg/l	0.762	0.756	0.875	0.900	0.888	0.783	0.871	0.870
Flash point	°C	40	54	50	68	78	68	4	25
KB value		31	26	87	91	63	26	105	95
Aniline point	°C	69	85	13.6 (M)	16.1 (M)	36 (M)	82	10 (M)	10 (M)
Colour	Saybolt	+30	+30	+30	+30	+30	+30	+30	+30
Evaporation rate (nBuAc = 1)		0.19	0.10	0.25	0.07	0.008	0.01	2.0	0.76
Viscosity at 25°C	mPas	0.87	1.40	0.79	1.07	1.61	1.60	0.55	0.60
Bromine index	mg Br/100 g	< 50	—	—	—	—	—	—	—
Aromatics	% m/m	< 0.5	< 0.5	99*	99.5*	74*	2.5*	99.9*	99.8*

(M) = mixed aniline point.
* % v.

TABLE IV
Relative Evaporation Rates

Solvent	Evaporation rate n-butyl acetate = 1
Hexane	7.2
Cyclohexane	4.5
SBP 80/110	4.27
Toluene	2.0
SBP 100/140	1.9
Xylene	0.76
White spirit	0.19
White spirit (115°F flash)	0.12
Shellsol AB	0.06

(ASTM D611), which determines the minimum equilibrium solution temperature for equal volumes of aniline and solvent, in other words, the temperature at which two phases just become miscible—n-heptane is used as a standard at 69.3 ± 0.2°C. Aromatic hydrocarbons give very low temperatures such that aniline can crystallize from the mixture, and consequently the mixed aniline point (ASTM D611) is used then. This is the minimum equilibrium solution temperature of a mixture of two volumes of aniline, one volume of solvent and one volume of n-heptane. The most powerful solvents have the lowest aniline/mixed aniline points. Not surprisingly, there is a relationship between the aniline and mixed aniline points; this is shown in Fig. 3.

(ii) *Kauri-butanol number.* Perhaps the best known criterion of hydrocarbon solvent power is the Kauri-butanol number (ASTM D1133), which is quoted in most literature, together with the (mixed) aniline point. Basically, it is a measure of the tolerance to added hydrocarbon diluent of a standard solution of kauri resin dissolved in n-butanol. Standards are toluene (KB = 105) and 75% v n-heptane plus 25 per cent toluene (KB = 40). A high KB number implies that the solution will tolerate large quantities of the hydrocarbon before resin precipitates from solution, and this is indicative of a high hydrocarbon solvent power.

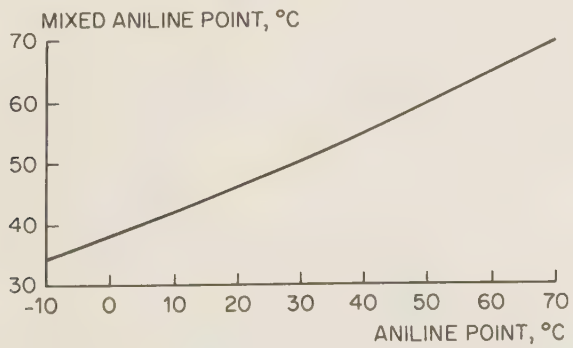


Fig. 3. Relationship between the aniline and mixed aniline points.

Commercially available solvents have KB values ranging from about 25 to 105. The relationship between aniline point and Kauri-butanol number as shown in Fig. 4 is reasonable for all solvents except those of high aromatic content.

(c) Appearance and Colour

All solvents should be clear and free from suspended matter, and with the exception of a few very high boiling products, hydrocarbon solvents are water white.

A widely used colour scale is the Saybolt scale. For many products a typical value is greater than +30 on this scale, which is the highest reading obtainable by the test. Good colour is regarded as a quick guide to purity, since both contamination and oxidation generally lead to colour deterioration.

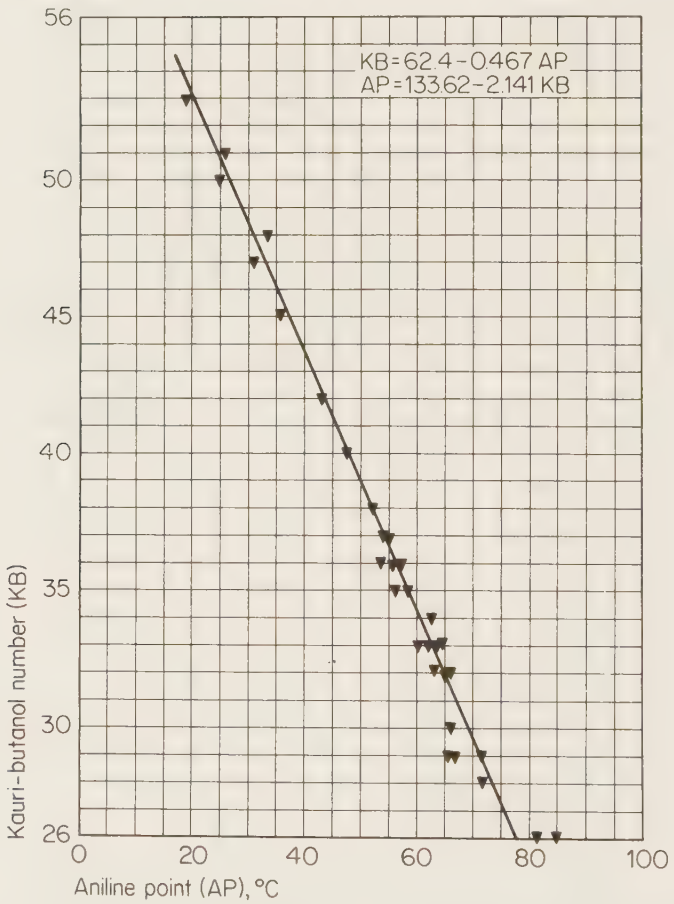


FIG. 4. Solvent power: KB number/AP relationship for medium to zero aromatic content solvents.

(*d*) *Odour*

This property of a solvent is becoming increasingly important as odour is often, wrongly, associated with hazard. It is an extremely subjective property and is therefore very difficult to measure scientifically. The most disagreeable odours in hydrocarbons are due to impurities such as sulphur or oxidized degradation products. Sulphur can be present in a low odour form, but in end-uses where solvent emissions are burnt an objectionable smell will be apparent at the stack. The composition of the solvent also gives hydrocarbons their characteristic odour; most people find that aromatic hydrocarbons impart a sharp unpleasant odour. Naphthenes by contrast have a much lower and sweeter odour. Isoparaffins may be considered odourless.

In closed industrial systems odour is often not important; however, in end-uses, such as photocopying, degreasing, low-odour paints, and household products, odour is very important.

(*e*) *Viscosity*

Hydrocarbon solvents have low viscosities. In any class of hydrocarbons, as the density and boiling range of the solvents increase the viscosity increases.

Vapour Pressure

A knowledge of solvent vapour pressures is important in many areas of solvent application; it is sometimes necessary for determining which solvents may be used in various applications, and in what proportion in blends. This is often the case when distillation, recovery or high temperature extraction is part of a solvent-using process or application.

The vapour pressure P (in mmHg) of a solvent at a temperature T (°C) can be expressed by the Antoine equation:

$$\log P = A - \frac{B}{T + C}$$

where A, B, and C are constants characteristic of the solvent. This relationship is applicable over a wide range of temperatures to a fair degree of accuracy and, if A, B, C, and T are known, these values can be substituted into the equation to yield the vapour pressure. Table V presents data for some commercially available hydrocarbon solvents. The Antoine constants for these solvents have all been experimentally derived and can be applied over a wide temperature range. Caution should be exercised if the equation is used to predict the vapour pressure of mixed solvent systems, because these can deviate quite markedly from ideal behaviour.

Component Composition

In terms of the number and type of chemical molecules present, hydrocarbon solvents are extremely complex materials. For products with final boiling points up to about 100°C it is possible to identify and quantify all the components present. This is achieved using high resolution capillary column gas chromatography.

TABLE V
Antoine Constants of Hydrocarbon Solvents

Solvent	Temperature range (°C)	Antoine constants		
		A	*B*	*C*
n-hexane	−10/110	6.878	1171.5	224.31
n-heptane	15/130	6.902	1268.1	216.9
Cyclohexane	30/70	6.867	1216.9	224.53
SBP 65/70	25/65	7.487	1557.9	273.15
White spirit	40/160	7.04	1830.3	273.15
Toluene	20/200	6.91	1211.0	220.79
o-xylene	63/145	7.00	1478.2	214.07
m-xylene	60/140	7.01	1463.2	215.16
p-xylene	60/139	6.99	1453.7	215.32
Shellsol A	40/140	7.81	2032.2	250.2
Shellsol AB	40/140	8.62	2668.4	283.9

A typical chromatogram for SBP 2 is shown in Fig. 5 and the component composition is given in Table VI.

For products with a higher final boiling point it is very difficult to identify all the components present. Figure 6 demonstrates the complex nature of the components present in white spirits. To give an indication of performance it is more usual to analyse hydrocarbons for total paraffins, naphthenes, and aromatics, rather than attempt an individual component analysis.

TABLE VI
Component Composition of SBP 2

Component	% wt
n-C_5	0.04
cyC_5	0.05
2,3-dime C_4	0.21
2-me C_5	2.34
3-me C_5	4.63
n-C_6	30.38
mecy C_5 + 2,2-dime C_5	9.70
2,4-dime C_5	2.17
3,3-dime C_5	0.32
cyC_6	11.70
2-me C_6	10.02
1,1-dimecy C_5 + 2,3-dime C_5	4.80
3-me C_6	9.17
1-*cis*-3-dimecy C_5	1.69
1-*trans*-3-dimecy C_5	1.21
1-*trans*-2-dimecy C_5 + 3-eth C_5	3.01
n-C_7	6.62
mecy C_6	1.32
Rest (ind. olefins)	0.08
Bromine index mg Br/100 g	20
Olefins (calculated from the bromine index), % wt	0.01

n- = normal-; me = methyl; cy = cyclo; C = carbon; C + number = number of carbon atoms in the molecule; eth = ethyl.

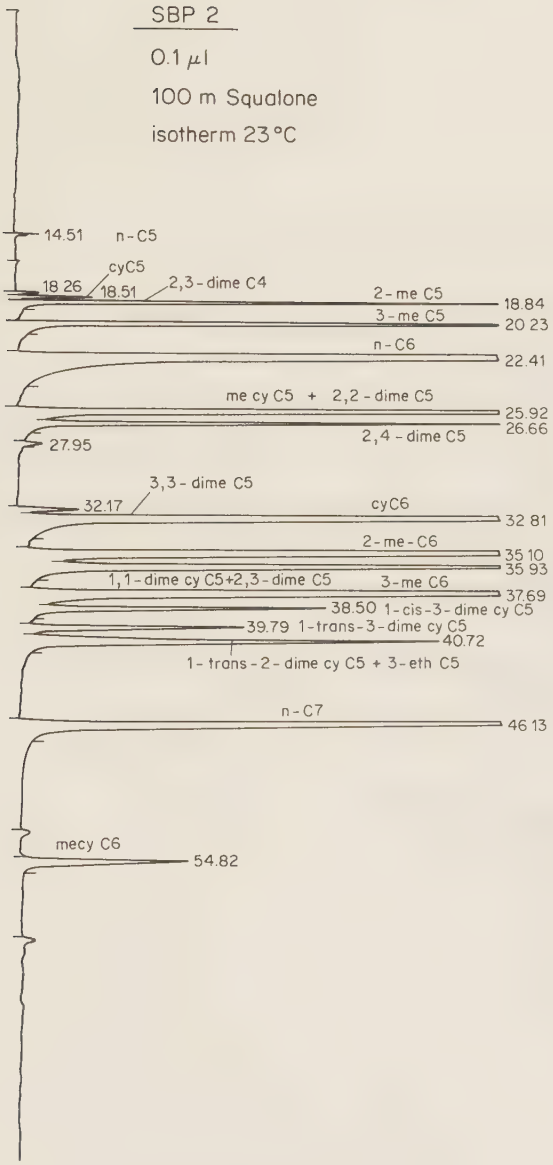


FIG. 5. Chromatogram of SBP 2.

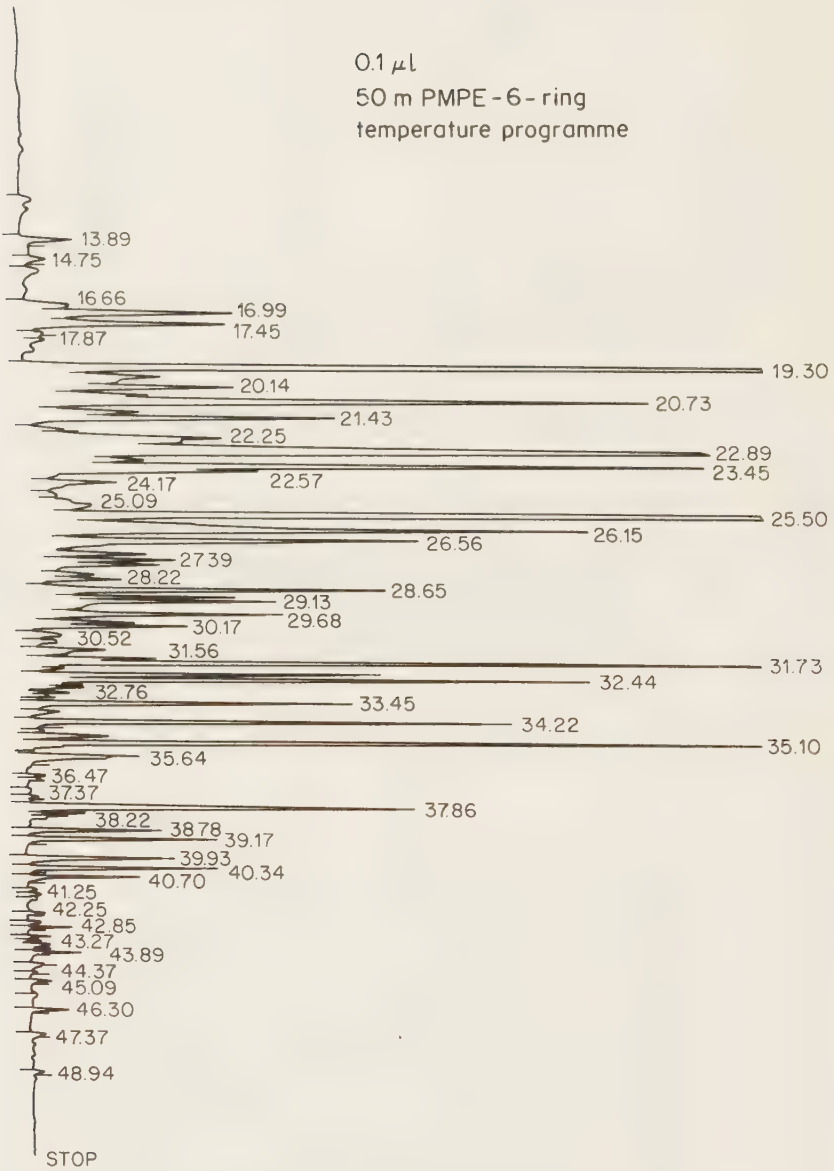


Fig. 6. Chromatogram of white spirit.

A multi-column gas chromatograph is available which is designed to separate aromatic, naphthenic, and paraffinic components in hydrocarbon solvents which boil up to 200°C. This P.N.A. analyser is manufactured by Packard-Becker under Model Number 411. It consists of three columns, a polar, a non-polar, and a molecular sieve. The first two are used to separate the aromatics from the saturates and the third to separate the naphthenes from the paraffins. Using a series of switching valves it is possible to separate the components of the solvent according to type and carbon number. A typical analysis of white spirit is shown in Table VII.

For solvents with end points above 200°C the fluorescent indicator method provides a useful guide to composition. In this method, a sample of the solvent containing traces of an added fluorescent dye mixture is introduced into a small glass adsorption column with a long narrow extension. The column is packed with fine activated silica gel. When the sample has been adsorbed on the gel, alcohol is added to desorb and force the sample down the column. The hydrocarbons are separated, according to the adsorption affinities, into aromatics (including aromatic hydrocarbons with olefinic side chains, as well as any sulphur, nitrogen, and oxygen compounds), olefins, and saturated hydrocarbons. The fluorescent dyes are also selectively separated with the sample fractions and make the boundaries of the aromatics, olefins, and saturated hydrocarbons clearly visible under ultraviolet light. The volume percentage of each hydrocarbon type is then determined by measuring the length of each zone in the long narrow extension of the column.

TABLE VII

P.N.A. Analysis of White Spirit (100°F)

Component	% wt
A_6	<0.1
A_7	<0.1
A_8	1.0
A_9	11.8
A_{10}	4.3
A_{11+}	2.0
N_7	<0.1
P_7	<0.1
N_8	0.4
P_8	0.5
N_9	6.3
P_9	10.8
N_{10}	10.7
P_{10}	31.2
N_{11}	4.7
P_{11}	13.5
N_{12}	0.4
P_{12}	2.3

A = Aromatic component.
N = Naphthenic component.
P = Paraffinic component.
Subscript = the number of carbon atoms in the compound.

Although olefins are usually present in hydrocarbon solvents only at very low levels they have a marked negative effect on solvent performance in certain end-uses, e.g. polymerization media. The degree of unsaturation of a solvent is usually measured by the consumption of bromine under standard conditions. The bromine index is defined as the weight, in milligrams, of bromine absorbed by 100 g of sample. Hydrocarbon solvents rarely have a value greater than 200 mg/100 g, and those manufactured by the hydrogenation route have values of less than 50 mg/100 g.

USES OF HYDROCARBON SOLVENTS

The end-uses of hydrocarbon solvents fall broadly into three basic categories depending on the function of the solvent in that end-use:

(a) Surface coatings—here the function of the solvent is to lay down a thin film of a polymer, on some particular substrate, after which it evaporates, e.g. paints, printing inks, adhesives, etc.
(b) Extraction processes—here the function of the solvent is to extract selectively some particular ingredient from a mixed product or raw material, e.g. vegetable oils, pharmaceuticals, cleaning and degreasing, etc.
(c) Chemical processes—here the function of the solvent is as an inert reaction medium or catalyst carrier, e.g. in polyolefin manufacture.

Extraction and chemical processes end-uses are invariably accompanied by solvent recovery, an important factor in the choice of solvent. In surface coatings recovery is less common.

Surface Coatings

Paints, lacquers, and printing inks can be grouped together under the name of surface coatings. The surface coatings industries are by far the largest users of petroleum hydrocarbon solvents, including almost every available type. Because of the long history of the use of coatings materials, the terms employed are often loosely defined and inconsistently used. The word 'paint' is usually applied very broadly to cover pigmented materials. Non-pigmented paints are often termed varnishes. A familiar example of paints is the 'oil paint' widely used in house decorating which is, in fact, based on a combination of vegetable oil and synthetic resin. Chlorinated rubber paints are used where higher chemical or water resistance is required. Bituminous paints, based on cut-back bitumens (see Chapter 29), do not contain pigment as such, the bitumen providing the colour. In these systems the resin (binder) is soluble in the hydrocarbon used, and oxygenated organic solvents are usually absent.

Stoving paints are hardened (cured) by heating, the usual temperatures employed being between 100 and 200°C. Various resins, mainly synthetic, are used as binders. In most cases the predominant solvent used is of a hydrocarbon type, but a proportion of an oxygenated organic solvent, commonly n-butyl alcohol, is present.

Lacquers are usually defined as systems which dry purely by solvent evaporation, that is without chemical reaction. Lacquers are sometimes pigmented, for example the nitrocellulose lacquers used in repairs to motor

cars, and sometimes unpigmented, for example, the clear lacquers used in furniture finishing. Because no chemical change takes place during drying, it is usual to choose a resin which is insoluble in the commoner organic liquids, such as white spirit or ethyl alcohol. Examples are nitrocellulose, vinyl resins (vinyl chloride/vinyl acetate co-polymers), and non-reactive acrylic resins. Although hydrocarbons are non-solvents, they form useful constituents of the complex solvent mixture used. For example, they may be added to reduce the solvent attack of one coat on another or merely to reduce cost.

Choice of Solvent

As a generalization, the chemical type of solvent used, for example, aromatic or aliphatic hydrocarbon, ketone or alcohol, is decided by the type of resin involved, and the desired viscosity. Solvents tending to give low viscosity are commonly said to have high solvent power. The volatility of the solvent, however, is mainly decided by the way in which the paint is to be applied; for example, a relatively 'slow' solvent like white spirit is used to allow time for 'laying off' when brushing, but a relatively 'fast' solvent such as toluene will be included to avoid 'sagging' when spraying.

As mentioned earlier, solvent power is mainly dependent on the aromatic/non-aromatic content. The aromatic content is therefore a commonly quoted property. However, as different aromatic compounds have different solvent powers and in de-aromatized products naphthene content is important, the Kauri-butanol number is commonly used as an aid to solvent selection.

Both volatility and solvent power may have a marked effect on the appearance of the final coating, particularly on the way paint films flow to give what should be a smooth even surface. Rapid drying and high viscosities may cause unevenness or leave brush marks, whereas low viscosities or slow evaporation may contribute towards sagging, i.e. the paint runs down vertical surfaces. Some paints dry by evaporation of the solvent alone, chlorinated rubber is an example, and hence the solvent will re-dissolve the paint film at any time. Thus, the solvents present in a second coat of paint will tend to re-dissolve part of the first coat, no matter how long this has been left to dry. This may cause difficulties if the second coat is applied by brushing, especially if the paint contains a strong solvent.

Most paints dry not only by solvent loss, but also by chemical change in the film-forming material, that is by polymerization. The best known types are air-drying paints, based on drying oils such as linseed combined with natural or synthetic resins, the commonest of these being alkyd resins. When the solvent has evaporated, paint films of this type continue to form by polymerization. If a second coat is applied at an early stage, before polymerization has advanced very far, the first coat may be partially re-dissolved. At a somewhat later stage of polymerization, the solvent may cause the resin to swell so that re-coating may give rise to blistering and lifting of the paint film. When polymerization is more advanced, solvents in the second coat will have no effect, and re-coating difficulties are avoided. Aromatic solvents are more likely to cause lifting than are aliphatics, and hence the widespread use of the ordinary grade of white spirit containing 15–20 per cent aromatics. This has enough solvent power to dissolve a reasonably wide range of resins, giving solutions with an acceptable

viscosity, but does not give lifting in correctly formulated oil paints used under normal conditions.

The solubility of these types of resin in hydrocarbon solvents depends largely on the ratio between resin and oil. Where the oil content is considerably greater than the resin content, the formulation is described as 'long oil', and is soluble in low aromatic hydrocarbon solvents. On the other hand, where the proportion of oil is lower, that is in 'short oil' resins used particularly in stoving enamels, a highly aromatic solvent is required. In these stoving enamels xylene is widely used, but more recently the advantages of slower-evaporating aromatics solvents such as the highly aromatic white spirits, have been realized, especially with regard to improved flow. With stoving paints, lifting cannot occur since the second coat is applied either before stoving ('wet-on-wet' technique) or after stoving, in which case polymerization has made the first coat insensitive to solvent attack. Thus mainly aromatic hydrocarbon solvents are used, since these tend to give a lower viscosity.

Since aromatics usually have the strongest odours, there has also been a trend in the reverse direction for household and similar paints. White spirits with a very low or nil aromatics content, are used to give low odour or odourless paints. However, the odourless white spirits, which are isoparaffinic in composition, have low solvent power. In some cases low solvent power gives a distinct advantage, for instance in certain thixotropic or 'gelled' paints, and more especially in flat wall paints designed to give a uniform coating on surfaces of variable porosity, such as plaster.

Because lacquers dry solely by evaporation, they present different solvent problems. The solvents for cellulose, vinyl, and acrylic lacquers are ketones, esters, and ether alcohols in conjunction with hydrocarbon solvents and, in some cases aliphatic alcohols. The quantity of hydrocarbon diluent which in practice may be incorporated is higher in the case of aromatic solvents, as these show less tendency to increase the viscosity of the formulations compared with aliphatic solvents. Volatility is critical, since a correct balance between the different components in the solvent system during evaporation must be maintained. For example, in a cellulose lacquer, if the hydrocarbon diluent evaporates more slowly than the other components, a point is likely to be reached where the resins are precipitated. This is termed 'cotton blush' in the case of nitrocellulose, or 'resin blush' when one of the other resins present is precipitated. Too rapid evaporation of the diluent or other other solvents can cause chilling which may allow moisture to be deposited on the film, to give what is known as 'water blush'. Correctly formulated solvent mixtures will not show these defects in normal conditions of use. One of the main advantages of these lacquers is their short drying time, and hence quite volatile solvents are chosen, and the hydrocarbon diluent must match this volatility. Thus SBPs of suitable boiling ranges may be used, those with high aromatic content having advantages. Toluene and xylene are similarly employed.

Extraction of Oil Seeds and Other Natural Products

These processes are examples of extractive uses of hydrocarbon solvents, and have much in common with degreasing and dry cleaning, described later.

The most important of these processes is the extraction of vegetable oils.

These oils provide a valuable source of food as well as raw materials for soap and paint manufacture. The solid by-product from oil seed extraction is rich in protein content, and is capable of use not only for animal feed, but indeed also for conversion into protein-rich food supplements for human consumption.

Whilst a large variety of seeds are extracted (including, surprisingly, grape pips), only about a dozen or so are of major commercial world importance. These include soya beans, sunflower, ground nuts, castor, cotton seed, olives, and rice bran.

Traditionally these oils were extracted by mechanical methods employing either hydraulic presses or screw expellers. Although the latter are more efficient, mechanical methods may leave 5–10 per cent of oil in the residual cake, which cannot be pressed out without severe thermal degradation of the oil and cake. The use of solvent extraction readily permits more than 99 per cent of the oil to be extracted, and enhances the value of the by-product cake.

After suitable preparation (decorticating, cleaning, 'cooking' and flaking) some seeds may be directly extracted. More commonly, the suitably prepared seeds are subjected to a light pressing to reduce the oil content to below about 20 per cent. The pressed cake may then be further processed in solvent extraction plant to extract the remaining oil. Various kinds of plant of the batch or continuous type may be used, but in all cases the solvent is brought into contact with the prepared seeds or seed cakes for an adequate period, and drawn off when all the oil is dissolved.

Since the solvent is recovered from the oil by distillation, it should be fairly low boiling. The final boiling point of the solvent will sometimes be decided by the ease with which it can be distilled off from the extracted materials, some of which may be damaged or reduced in quality if the temperature becomes excessive.

A lower final boiling point can also reduce both the time and cost of the recovery process, depending on the amount of heat, usually in the form of steam, which has to be employed. However, a relatively high initial boiling point is necessary to minimize solvent vapour losses. The solvent used must also be selective for the oil and dissolve the minimum of unwanted pigments, resins, etc. occurring in the seeds.

The Ministry of Agriculture, Fisheries and Food (MAFF) publish purity criteria for a general hydrocarbon solvent. This is shown in Table VIII.

Because of economic factors, a much narrower boiling fraction is used, and SBP 65/70 (commercial hexane) which complies with this specification is the preferred solvent.

Two other solvent extraction outlets which require the use of very low-boiling solvents, are perfume extraction and pyrethrum extraction. In both cases, the desired substances are present in flower petals, and by contacting with iso-hexane or a similar low-boiling SBP, the perfume or pyrethrum dissolves in the hydrocarbon solvent and may be recovered by carefully evaporating the solvent, taking care to apply as little heat as possible to avoid damaging the delicate raw material. Whereas solvent losses during oil seed extraction are usually well below 1% wt of raw material treated, in the case of perfume extraction, the losses will usually be somewhat higher.

Solvent extraction is often employed in the production of fats from by-products. In some cases, the solvent is chosen with a distillation range

TABLE VIII
MAFF Specification

Synonyms	Petroleum spirit, petroleum ether, essence, aliphatic hydrocarbons
Description	A clear, colourless, mobile, highly flammable liquid with a characteristic petroleum-like odour; free from sediment and suspended matter
Content	Shall consist of mixtures of saturated hydrocarbons containing 5, 6, 7, and 8 carbon atoms, the majority of which are acyclic
Distillation range	Shall distil completely between 25 and 105 °C
Residue on evaporation	Not more than 20 mg per kg
Benzene	Not more than 0.05% m/m
Aromatic hydrocarbons	Not more than 0.2% m/m
Polycyclic aromatic hydrocarbons	The following absorbance limits per cm of optical path length shall not be exceeded wavelength (nm) — absorbance 280–289 — 0.15 290–299 — 0.12 300–359 — 0.08 360–400 — 0.02
Sulphur	Not more than 10 mg per kg
Lead	Not more than 1 mg per kg
Arsenic	Not more than 1 mg per kg
Unsaturated hydrocarbons other than aromatic hydrocarbons, bromine index (mg of Br per 100 g)	Not greater than 200

somewhat higher than that of hexane, so that it acts also as an azeotroping agent.

The solvent dewaxing of lubricating oils in which toluene is commonly used, is described in Chapter 26.

PRINTING INKS

Printing inks vary according to the method of printing, the type of printing press, the speed of operation, and the properties of the paper or other material on which printing is carried out. Solvent requirements are, therefore, frequently influenced by these factors in addition to most of the factors mentioned in connection with paints and lacquers.

There are four main printing methods: lithographic, letterpress, gravure, and silk screen.

In the first method, the design is traced on a metal plate with a greasy material, the remainder of the plate being coated with gum. Damp rollers are passed over the plate, water being absorbed by the gum, but repelled by the grease. Inked rollers are then passed over the design and the ink is repelled by the water but accepted by the greasy zones. Printing may then take place directly on to paper or, more usually, indirectly on to a rubber-covered cylinder and thence on the paper; this is the 'offset' lithographic process. Lithographic inks are normally based on drying oils that have been 'bodied' by heating. The solvent must clearly be immiscible with water and, in the offset process, should not be highly aromatic, as this would affect the rubber 'blanket'. Hydrocarbon solvents are also used for blanket washes.

Letterpress printing takes place from raised type or plate with a pattern in relief. Many letterpress inks are basically similar to lithographic inks. Traditional news inks usually consist of pigment, for example carbon black, dispersed in a mineral oil vehicle of suitable viscosity. Such inks dry essentially by absorption into the paper, leaving the pigment at or near the surface. More modern high-speed printing processes use the so-called heat-set or quick-set inks which contain not only pigment, but also suitable resin binders which readily precipitate during the drying of the ink film. For such inks, the solvent is usually one of the narrow-cut kerosine solvents of low aromaticity, specially designed for this outlet. If more volatile solvents than these were used in letterpress or lithographic offset printing, the inks would dry out prematurely on the presses and rollers.

Gravure printing is from an engraved surface, and boiled drying oils are sometimes used as the basis for the inks. However, in the reproduction of photographs and in the printing of high-gloss magazines, the gravure process, known as photogravure, uses various resins, including nitrocellulose, in conjunction with hydrocarbon solvents, particularly toluene and xylene. As the solvents in the photogravure process are relatively expensive, solvent recovery is frequently practised by passing the air containing the vapour over carbon beds, from which adsorbed solvents are later recovered by steaming.

In silk screen printing, a stencil design is laid down on a stretched screen of silk, nylon, or fine metal mesh. Ink, of a paint-like consistency, is forced through the screen by a squeegee on to the substrate. Silk screen printing inks closely resemble paint in their formulation, and hence high boiling SBPs, for example SBP 6 and white spirit, are very suitable solvents.

RUBBER AND ADHESIVES

Hydrocarbon solvents are used in many sectors of the rubber industry, beginning with the preparation of natural rubber for shipment. To prevent natural rubber bales from sticking to each other, they are coated with a fine white powder. White spirit of 15 or 45 per cent aromaticity is used in the preparation of suitable bale coating solutions.

The main uses of hydrocarbons in the rubber industry are, however, found in the production of adhesives and in the manufacture of tyres.

Adhesives play a vital role in a broad range of manufacturing processes: clothing and footwear, automobiles, the building industry, furniture and other consumer durables and, of growing importance, the packaging and labelling industry.

Wherever a relatively low-cost water-resistant adhesive is needed, a rubber-based adhesive may well provide the answer.

Rubber doughs and cement made from natural rubber, SBR and other hydrocarbon rubbers, are commonly made up by placing compounds of these rubbers in tanks containing SBPs. The rubber absorbs several times its own weight of solvent to give a sticky solution which may be stored and later used as an adhesive. Rubber cements are usually vulcanized after application.

The choice of solvent is mainly a question of volatility, dictated in turn by the type of adhesive required, i.e. whether fast drying or slow drying. For natural rubber the composition of the hydrocarbon solvent is not usually very

important, and aliphatic SBPs may perform just as well as toluene and non-hydrocarbon solvents.

For adhesives based on more specialized polar rubbers, for example chloroprene and nitrile rubbers, aliphatic hydrocarbon solvents are unsuitable on their own.

During tyre production, a medium- to high-boiling SBP may be used to increase the tackiness of the successive layers of rubber and rubberized fabrics from which tyres are built up.

POLYMERIZATION PROCESS REACTION MEDIA

Hydrocarbon solvents are widely employed in the chemical industry as reaction media during the polymerization of ethylene, propylene, and other olefins to form plastics and elastomers. The function of the hydrocarbon solvent differs from one process to another.

High-density polyethylene, polypropylene, and certain olefin elastomers are manufactured at medium pressures and temperatures by processes employing heterogeneous catalysts. Usually a catalyst is introduced into the reactor as a suspension of slurry in the hydrocarbon solvent. At the same time, the hydrocarbon acts as a solvent for the monomer. When reaction takes place, the polymer is formed either as a suspension of small polymer particles, or as a polymer solution. The choice of solvent is one factor deciding which type of polymer is formed. The hydrocarbon solvent helps to lower the viscosity of the reaction products, and is extremely useful in controlling the reactor temperatures by taking up some of the heat of reaction.

After the polymer is formed, it is removed from the solvent by centrifuging, or by flashing off the solvent, which is recovered and recycled after purification.

A most important requirement is that the hydrocarbon solvent should be free from polar impurities, in particular water, sulphur compounds, and other volatile compounds of oxygen, nitrogen, chlorine, etc. Olefins should also be absent and a very low aromatic hydrocarbon content is desirable. Some of the impurities mentioned, if present, may easily poison the catalyst system, and others interfere with the course of polymerization.

Where it is desired that the polymer should be formed as a suspension, the choice of solvent will tend to be a low-boiling SBP, for example, pentane or hexane. Where the polymer is formed in solution, the solvent may be cyclohexane or a higher boiling SBP or white spirit, in all cases essentially aromatic-free.

In the case of low-density polyethylene, which is usually manufactured using oxygen or organic peroxides to initiate the polymerization reaction, the solvent, if used, may serve as a carrier for the peroxide catalysts, as well as assisting in the removal of heat from the reactor. Generally speaking, highly refined mineral oils are used as peroxide carriers. However, isoparaffinic and certain highly refined white spirit or kerosine solvents are preferred in some instances.

POLISHES

Polish has been an important outlet for solvents for many years. The early paste polishes were made simply by dissolving beeswax in wood turpentine. The

purpose of the solvent was merely to aid spreadability prior to buffing to a fine gloss. As beeswax is somewhat soft, other natural waxes were often added, such as Carnauba and later synthetic waxes derived from petroleum, e.g. microcrystalline wax, to give increased hardness and better wear properties. These formulations are still used as 'Antique' polishes, although for general furniture and shoe polishes, etc. turpentine has been replaced by white spirit and beeswax by paraffin waxes. The mild odour, controlled volatility, and solvent power make 'white spirits' very suitable for mixed waxes used in paste and cream form.

Recently, the types of polishes available have dramatically expanded. Aerosol products with combined polishing and cleaning properties have been introduced and many emulsion-based formulations are available.

The concentration of a solvent in a polish varies tremendously, depending on type. It can be as high as 70 per cent in a paste to almost zero in polymer/wax water-based emulsions. Some of the newer formulations contain oxygenated solvents of the glycol ether type as well as hydrocarbons.

To enable a thin film of wax to be applied, the solvent must obviously have sufficient solvent power to dissolve the wax. The solvent power should not, however, be so high that it attacks the surface coating of the object. The boiling range is also important in terms of evaporation which provides an ideal buffing interval.

MISCELLANEOUS USES

Other end-uses for hydrocarbon solvents are many; it is probably true to say that there are more end-uses than solvent grades. Many are not spectacular in terms of technology, but are consumers of large volumes of hydrocarbons; examples are metal degreasing, electronic component cleaning, car-dewaxing, and industrial dry cleaning. Some hydrocarbons are used as speciality fuels and as carriers for fuel additives and markers. In the household product area, where low odour is essential, very low aromatic 'white spirits' are used as barbecue lighter fluids, in decorative lamp oils, etc. Hydrocarbon solvents are often an essential ingredient in household toiletries, pre-cleaning formulations, etc. The choice of solvent is, as discussed earlier, dependent on solvent power needs, odour, and evaporation rate.

Some end-uses, although not large in terms of total consumption, are very important for particular groups of hydrocarbon solvents. Photocopying, for instance, is a very important end-use for certain isoparaffinic solvents. The process of wet photocopying requires a solvent which is odourless and which has a position in the boiling range to enable the solvent to dry completely during the copying process.

New hydrocarbon solvent end-uses are developed from time to time, which often require a new solvent, or a 'tailor made' blend. Recent instances are metal extraction from low-grade ores, heat set inks, and certain polymerization processes.

TOXICITY

The growing awareness of toxic hazards which may be posed by the presence of a wide variety of chemical substances in working environments, has made this aspect of hydrocarbon solvents more and more important.

For any solvent to have a systemic toxic effect it must first enter or contact the body. This it may do through the lungs by inhalation, through the mouth by ingestion, into the lungs by aspiration, and through contact with the eyes and skin.

Toxic effects in general may be separately considered as 'acute' and 'chronic'. Acute toxicity is the effect of a single dose and is of primary importance in connection with petroleum hydrocarbon solvents. Chronic toxicity is the effect of repeated exposure and, with some important exceptions (benzene and n-hexane), does not feature as a potential hazard in the case of petroleum hydrocarbon solvents. Benzene is believed to be unique among petroleum products in being capable of destroying the blood-forming elements in the body.

Inhalation Hazards

For volatile solvents, inhalation is usually the more important type of hazard, although hydrocarbon solvents as a class are amongst the least toxic of all commonly used organic solvents as regards acute inhalation hazards. However, benzene and SBPs containing appreciable amounts of benzene may present a serious chronic hazard when their vapour is repeatedly inhaled by susceptible individuals over a long period of time.

For a small minority of people, over-exposure to benzene vapour may result in the development of an irreversible blood disease which in extreme cases could prove fatal. For this reason, the use of benzene as an industrial solvent is strictly restricted in a number of countries. In the case of n-hexane, gross chronic over-exposure can result in peripheral neuropathy.

For hydrocarbon solvents in general, as for nearly all organic solvents, excessive inhalation of the vapour should be avoided. This is achieved by the provision of efficient ventilation systems in workshops and factories, particularly for confined work areas. A most effective system which is especially to be recommended is that referred to as spot ventilation, i.e. a directed air stream, away from the work area, which removes the vapour from the spot at which it is liberated and thereby removes it from the working area. General ventilation, except in a few circumstances, such as working in the open air, is frequently insufficient to maintain an air concentration below the threshold limit.

Threshold Limit Values

The American Conference of Governmental Industrial Hygienists (ACGIH) annually publishes a list of recommended Threshold Limit Values (TLV) for chemical substances. Threshold Limit Values are time-weighted average concentrations for a normal 8-hour work-day and a 40-hour work-week to which nearly all workers may be repeatedly exposed day after day without adverse effect.

The notation 'skin' is used to indicate products for which the TLV is invalidated unless precautions are taken to prevent its absorption through the skin or mucous membranes.

A few recommended TLVs published in 1982 for hydrocarbon solvents are

TABLE IX
Recommended Threshold Limit Values (1982)

Hydrocarbons	ppm*
Benzene†	10 (A2)
Cyclohexane	300
Ethylbenzene	100
n-Heptane	400
n-Hexane	50
Hexane (other isomers)	500
Methylcyclohexane	400
Octane	300
Pentane	600
Stoddard solvent (White spirit)	100
Toluene	100
Turpentine–skin	100
Xylene (o, m, and p)–skin	100

* Parts of vapour per million parts of contaminated air by volume, at 25°C and 760 mmHg pressure.

† A2. Industrial substances of carcinogenic potential for man.

shown in Table IX. The AGICH publication incorporating the list of TLVs should be consulted for more detailed guidance on their interpretation.

In the UK TLV values are also listed in annual issues of the Health and Safety Executive Guidance Note EH 15, giving also notification of any intended changes (HMSO).

Oral Ingestion and Aspiration

Oral ingestion is unlikely to be a serious problem for the more volatile hydrocarbon solvents. Accidental ingestion of white spirits and kerosine solvents is probably more likely to occur, particularly of products containing these solvents, for example, wax polishes.

Although the oral ingestion hazard as such is slight, there is a danger which may arise after accidental ingestion, namely aspiration if vomiting occurs. This is a particularly serious hazard with white spirits and kerosines. If, as is possible under these circumstances, the patient aspirates some of the product, as a liquid, into the lungs, thus causing chemical pneumonitis, it may be fatal. For this reason it is recommended that induced vomiting or gastric lavage is not carried out.

Eye and Skin Toxicity

Liquid hydrocarbon solvents splashed into the eye are moderately to slightly irritating, aromatics being rather worse than non-aromatics.

Because of their ability to dissolve natural fats from the skin, most hydrocarbon solvents can cause some degree of skin irritation, particularly if the exposure is prolonged. Aromatics are somewhat more irritating to the skin than the non-aromatic products, but the difference between them is much less pronounced than in the case of eye irritation.

STORAGE AND HANDLING

Many of the considerations on the problems of storage and transportation affecting oil products generally, and discussed in Chapters 32, 33, 36 and 37, also apply to hydrocarbon solvents, as do safety and similar regulations. Transport by pipeline is rare, except of course within plant and installation, since quantities are relatively small. Hydrocarbon solvents are shipped in bulk by tankers, barges, and road and rail tank cars. Smaller quantities are delivered in mild steel drums, usually of 200-litre capacity, returnable for the inland trade, but non-returnable in the case of exports. A small amount of trade may be done in containers down to as little as 20-litre cans.

In view of the requirements of the solvent trade it is important that special precautions are taken to avoid product contamination. So far as is possible tanks, lines, and pumps are kept segregated, and not used for other products. In particular, hydrocarbon solvents are not loaded immediately after heavy or black products, or leaded gasoline. When loading commences, samples should be taken and inspected, to ensure that no contamination has taken place.

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Lubricating Oils

By A. L. MILLS

INTRODUCTION

When two clean surfaces are in relative motion under an applied pressure, there are two factors of the greatest practical importance, both of which can be related to the degree of physical interaction that occurs between the surfaces.

First, a definite force is required to keep the surfaces in motion, the size of this force usually being a fraction of that keeping the surfaces in contact. The ratio of these forces is known as the coefficient of friction, and its value will be controlled by the nature of the two contacting materials, and the surface finish. Secondly, wear, or removal of material from the contacting surfaces, will take place, and again the nature of the surfaces controls the severity of this process under clean conditions.

In engineering practice the coefficient of friction at rubbing surfaces is of importance because of its influence on power and the development of heat, while the wear of those surfaces will control the life of machines and equipment.

Lubrication is the art of minimizing friction and wear by interposing between the rubbing surfaces a film of a further material, known as a lubricant, which may be gaseous, liquid, or solid. Efficient lubrication is achieved so long as, first, a positive separation of the surfaces is achieved under motion and load and, secondly, the shear strength of the lubricant film is lower than that of the material of the surfaces.

LIQUID LUBRICANTS

Liquid lubricants find the greatest favour in engineering applications because they readily provide separation of surfaces when correctly applied, and have a high cooling ability when circulated through the bearing area. This chapter is devoted to a discussion of the properties of those liquids currently used for lubrication and popularly called 'lubricating oils' or, more correctly, 'lubricants'.

Auxiliary materials, added to these liquids to enhance their properties in one direction or another to meet the requirements of special applications, are commonly employed. Known as 'additives', the more important of the numerous materials that have been proposed for this purpose will be referred to in the later sections.

The liquids available for use as lubricating media can be classified into three types: animal or vegetable oils; mineral oils; synthetic oils.

Animal or Vegetable Oils

Historically, such materials provided the first widely used lubricants, and indeed the derivation of 'oil' from 'olea', the olive, is a pointer to this. In the

main these products, which result either from 'rendering' animal matter or from expression from vegetable matter such as seeds, consist of mixtures of glyceryl esters of various fatty acids. The poor chemical stability of these fatty esters, exemplified by the ease of attack by atmospheric oxygen at slightly elevated temperatures, coupled with their relatively high cost, has led to their almost complete substitution by alternative materials as major ingredients in lubricants.

Castor oil is a vegetable oil which still forms the major component of some lubricants designed for special applications. Its continued use is made possible by the use of anti-oxidation additives, which limit the production of acids and polymeric gums from the oil in service.

Castor oil is largely composed of the glyceryl ester of ricinoleic acid and most of the attractive properties of the oil, such as its ability to provide low coefficients of friction, its high viscosity, its limited effect on natural rubber, and its relatively slow migration from hot metal surfaces, are traceable to the structure of this ester.

Palm oil, derived from the fruit of the oil palm, has enjoyed continuous popularity as a lubricant in the manufacture of tinplate. To some extent this is due to its early use as a flux, but even with the introduction of inorganic acid fluxes the oil has remained in service in the final rolling process. Considerable attention has been given to the production of cheaper palm oil substitutes, but only partial success can be claimed for these.

Whilst sperm oil found many applications in a number of lubricants, because of its good lubricating ability coupled with a reasonably good resistance to oxidation, its use is no longer favoured on the grounds of protecting endangered species. This lubricating property of sperm oil is related to its structure which is that of a liquid wax, being principally composed of fatty acid esters of cetyl alcohol. There are now many synthetic esters used world-wide as sperm oil substitutes.

While fatty oils alone find only limited use as lubricants, large quantities are still employed for 'compounding' with mineral oils when

(a) improved lubricating ability is required, for example in certain general machine lubricants or neat cutting fluids;
(b) the ability to emulsify with water is sought, for example in cylinder lubricants for reciprocating steam engines running on wet steam, rock drill oils, or marine stern tube lubricants;
(c) scourability by saponification is required, for example in certain textile oils.

Rape seed oil, lard oil, castor oil, palm kernel oil, fish oils, etc. have been commonly used in this way for many years, and thus can be claimed to be some of the earliest lubricating oil additives as previously defined. The modern use of the word 'additive', however, tends to exclude naturally occurring materials.

Mineral Oils

The lower cost of lubricating oils produced from petroleum makes these the most widely used of all the available lubricants.

The residue from atmospheric distillation of crude petroleum, when itself

distilled and fractionated under reduced pressure, yields lubricating oil stocks of various viscosities, the lightest oils coming from the top of the fractionating tower and the heaviest from the bottom. The distillates and residues reflect the general chemical make-up of the crudes from which they are derived, and not all crudes are equally acceptable for the production of good quality lubricating oils. Refining subsequent to distillation is almost always essential to provide lubricating stocks of sufficient purity, and for special applications. For example, oils derived from paraffinic crudes will require de-waxing to permit satisfactory fluidity at low temperatures; undesirable colouring matter must be removed by, say, filtration through activated clay to provide products of better stability; asphaltic, resinous, aromatic, and other unsaturated materials must be removed by a suitable process to provide stocks of high oxidation resistance.

With older 'conventionally refined' oils the then acceptable level of quality was obtained by sulphuric acid treatment. However, the limited degree of refining and improvement of lubricant characteristics provided by this process at economic treatment costs and yields, coupled with health and safety considerations, has led to the almost universal adoption of solvent refining techniques. Selective solution of asphaltic, aromatic, and other undesirable materials from oils is readily provided by a large number of solvents, various combinations of which give optimum performance with raw lubricating oils derived from different types of crude, including some of those found in the North Sea close to the United Kingdom.

The use of hydrogen as a refining medium has increased rapidly during the past 25 years. Initially, this involved mild treatment in the presence of a catalyst, and had the effect of improving colour and oxidation stability, and of reducing acidity and the contents of sulphur, oxygen, and nitrogen compounds. This 'hydrofinishing' was intended to replace the clay treatment stage incorporated in other refining processes. More recently, the process has been extended to much more intensive treatment, known as 'hydrorefining' or 'hydrotreating', involving the saturation of most of the aromatics present as well as the cracking of condensed structures, to produce stable lubricating oil fractions of very high viscosity index but lower viscosity than the feedstock.

Reference should be made to other chapters, for details of the refining techniques outlined above.

The hydrocarbons found in mineral oils are mainly of three general types:

(a) straight- and branched-chain paraffinic compounds;
(b) polycyclic and fused-ring saturated hydrocarbons based on cyclopentane and cyclohexane prototype ring structures, collectively known as naphthenes;
(c) aromatics, both mono and polynuclear, which are unsaturated ring structures.

The straight, long-chain paraffins are wax-like and therefore their concentration must be minimized, especially in those oils for application at low temperatures. On the other hand, branched-chain paraffins can be very desirable constituents in a lubricant because of their good stability and viscosity/temperature characteristics. The longer the side chains in the molecule, the more marked do these attractive features become.

These desirable properties still exist in those naphthenes in which the number

of rings per molecule is low, but the side chains and connecting links are long and paraffinic. With increasing ring condensation and shortening of the paraffinic chains, the viscosity/temperature characteristics of the hydrocarbons progressively worsen in respect of their suitability for lubricants.

The crude oils and the raw lubricating oils derived therefrom will contain hydrocarbons in which aromatic rings feature in the molecular structure. The sulphur, nitrogen, and oxygen contents of the fractions will be mainly associated with these rings, and since refining methods have as one aim the reduction of the content of aromatics, because of their poor oxidation stability, and other undesirable features, the concentration of these elements will also be markedly reduced. The crude oils and derived lubricating oils are frequently classified as paraffinic, mixed-base, or naphthenic but, since the bulk of the hydrocarbons present in each type are naphthenes, these terms can be misleading unless they are clearly understood to refer roughly to the relative proportions of paraffinic chains and saturated rings in the average hydrocarbon molecule in each oil.

More precise classification was provided by the hydrocarbon analysis technique proposed by Waterman, although with this method the exact identity of hydrocarbons cannot be established. Many other analytical techniques have subsequently been proposed. While all of these are useful for indicating the relative proportions of naphthenic rings, aromatic rings, and paraffinic chains in any given oil fraction, none is as precise as modern spectroscopic techniques and mass spectrometry.

The data in Table I are based on figures published by Schilling, and conveniently illustrate the points just discussed. In this table, C_P, C_A, and C_N refer respectively to carbon atoms in paraffinic, aromatic, and naphthenic form, and the table shows how relatively minor differences in the proportions of the carbon atoms associated with the various groups can greatly affect the properties of the refined oils. In base stocks from Pennsylvanian crudes, considered to be highly paraffinic, the C_P proportion can approach 80 per cent.

Table II, in which structural analysis is depicted in a different form, shows

TABLE I

Influence of Chemical Character on Some of the Properties of Lubricating Oils

	Naphthenic ex-USA crude, acid refined	Naphthenic ex-Venezuelan crude, acid and solvent refined	Paraffinic ex-Middle East crude, solvent refined and dewaxed
Density at 20°C	0.915	0.901	0.882
Viscosity, cSt			
at 40°C	139	132	76
at 100°C	10.6	11.2	9.3
Viscosity Index	34	58	97
Sulphur % wt	0.24	0.92	0.83
$\%C_P$	50	59	66
$\%C_A$	14	8	6
$\%C_N$	36	33	28

TABLE II
Solvent Refining versus Hydrorefining

	Undewaxed feedstock	Dewaxed raffinate solvent refined	Dewaxed raffinate hydrorefined
Composition, % wt			
Paraffins	8.8	4.5	8.8
Non-condensed naphthenes	30.6	49.0	60.0
Condensed naphthenes	14.6	25.3	21.0
Monocyclic aromatics	15.0	16.4	4.8
Condensed aromatics	31.0	4.8	5.4
	100.0	100.0	100.0
Density at 20°C	0.931	0.906	0.870
Viscosity, cSt			
at 40°C	602	500	55
at 100°C	33.2	31.9	8.22
Viscosity Index	85	95	119
Pour point, °C	54	−18	−18
Carbon residue (Ramsbottom), % wt	0.9	0.5	0.05
Sulphur, % wt	2.8	1.6	<0.05

the important effect of hydrorefining, as compared with solvent refining of the same feedstock, on both structure and properties for similar yields of approximately 50 per cent. The breakdown and the saturation of aromatics by hydrorefining are illustrated, as are the consequent fall in viscosity and the almost complete elimination of sulphur compounds.

Synthetic Oils

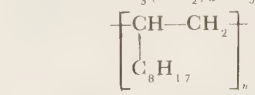
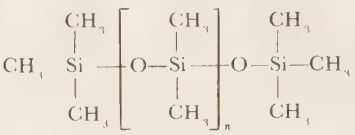
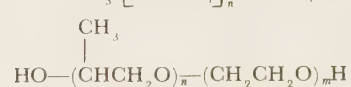
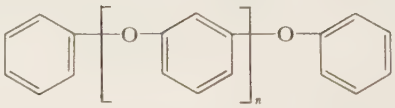
The importance which synthetic fluids are achieving as lubricants, especially in the aviation field, justifies a discussion of their nature and properties.

Lubricants produced by entirely synthetic means cannot, in general, compete with mineral oils on price and, indeed, some are at present extremely expensive. Accordingly, they find application only where full advantage can be taken of some property which mineral oils cannot match. Table III shows some

TABLE III
General Advantages of Synthetic Lubricants

Technical advantage	Applicational advantage
Reduced pour point	Lower operating temperatures
Superior oxidation stability	Higher operating temperatures
Higher viscosity index	Wider operating ranges
Superior dispersancy	Longer drain periods
Lower volatility	Reduced oil consumption
Better lubricity	Lower viscosity—energy saving
Clean burning	Specialist applications
Flame resistance	Fire resistance
Non-toxicity	Food contact

TABLE IV
Synthetic Fluids Used as Lubricants

Type	Structure
Hydrocarbons	$CH_3(CH_2)_nCH_3$
Polyalpha olefins	
Silicones	
Polyglycols	
Diesters	$C_{12}H_{25}OCOC_{10}H_{20}COOC_{12}H_{25}$
Complex esters	$C(CH_2OCOC_8H_{17})_4$
Phosphate esters	$(C_8H_{17}O)_3P{=}O$
Silicate esters	$Si(OC_{10}H_{21})_4$
Alkyl silicate esters	$(CH_3)_2Si(OC_{10}H_{21})_2$
Halogenated hydrocarbons	$CH_3(CH_2)_l(CHCl)_m(CH_2)_nCH_3$
Chlorofluorocarbons	
Polyphenyl ethers	

of the technical and applicational advantages of synthetic lubricants, whilst Table IV shows the principal classes and gives typical structural formulae.

Hydrocarbons

In the Fischer–Tropsch process, where a mixture of carbon monoxide and hydrogen is passed over or through a heated catalyst bed, a wide variety of hydrocarbon types can be produced. When the hydrogen proportion in the synthesis gas is high, paraffinic hydrocarbons predominate in the resultant hydrocarbons mixture, while for lower proportions of hydrogen, olefinic hydrocarbons are produced:

$$nCO + (2n + 1)H_2 \xrightarrow{\text{Catalyst}} C_nH_{2n+2} + nH_2O$$

$$nCO + 2nH_2 \xrightarrow{\text{Catalyst}} C_nH_{2n} + nH_2O$$

Lubricating oil fractions are not produced directly, but result from the catalytic polymerization of the olefinic fractions or of the olefins produced by cracking the more paraffinic hydrocarbons.

A number of other processes have been devised for the production of lubricant hydrocarbons, notably the polymerization of alpha olefins.

Silicones

A range of interesting fluids is produced by the polymerization of alkyl or aryl substituted siloxanes. The silicone fluids of commerce are usually polymethyl siloxanes, and in the specimen structural formula in Table IV, n can range between 1 and 13.

The outstanding features of these fluids are their very good viscosity/temperature characteristics, their low-temperature fluidity, and their relatively high flash points. However, under certain conditions these fluids exhibit rather poorer lubricating properties than do petroleum lubricants, and their cost is very high. Silicones of improved lubricity can be made by replacing some of the methyl groups by halophenyl groups.

Polyglycols

These fluids result from the reaction of aliphatic monohydric alcohols with certain alkylene oxides. The commercially available lubricants of this class are based mainly on propylene oxide and ethylene oxide. Polymers produced solely with the former oxide are virtually water insoluble, but copolymerization with mixtures of the two oxides gives water-soluble fluids. The molecular weights of the polymers of both types fall within the range 400 to 3000, the viscosity rising with rising molecular weight.

These fluids are quite attractive for certain high-temperature applications when suitably treated against oxidation, because depolymerization sets in at about 235°C, giving volatile fragments with a notable absence of carbonaceous residues.

In the main, the range of fluids provides products of good viscosity/temperature characteristics, of low pour point, and with densities very close to that of water. The water-insoluble polyglycols find their widest use in hydraulic brake fluids, while the water-soluble varieties are of special interest in fire-resistant hydraulic fluids.

Esters

A large number of esters and diesters have been proposed as lubricants, and in recent years the importance of this class of product has increased following their applicational success as substitutes, for example, for sperm oil. Among the most important are those diesters which result from the reaction of such dibasic acids as glutaric, adipic, azelaic, and sebacic acids with C_5 to C_{14} primary and secondary alcohols, branched-chain primary alcohols generally being preferred. A group of low-viscosity, chemically-stable lubricants can be produced which show excellent viscosity and volatility characteristics over a wide temperature range, which makes them particularly attractive for aircraft gas-turbine applications. Di-(2-ethyl hexyl) sebacate has been widely used as a base fluid, and Table V shows the typical physical characteristics of this fluid.

More recently, complex esters such as the 'hindered' neo-pentyl polyol esters have found wide application in aircraft gas-turbines. They have an approximately 40°C advantage in thermal stability over the diesters such as di-(2-ethyl hexyl) sebacate though some of this advantage is lost owing to limitations in the

TABLE V
Properties of Di(2-ethyl hexyl) Sebacate

Viscosity, cSt	
at −40°C	1410
at −18°C	187
at 40°C	11.8
at 100°C	3.23
Viscosity Index	149
Pour point °C	< −55
Flash point (IP 36)°C	222
Density at 20°C	0.915

stabilities of the additives used with them. Optimum properties are often obtained from selected mixtures of these hindered esters, and typical figures for a suitable mixture are given in Table VI.

Phosphate esters have been used increasingly as fire-resistant lubricants, for instance in some compressors, and as hydraulic fluids. Their lubricating properties are comparable with those of mineral oils, and selected esters have reasonably high viscosity indices. Hydrolytic stability poses a problem which can, however, be overcome by selection. Alkyl aryl phosphate esters or mixtures of trialkyl and triaryl phosphate esters are extensively used as aircraft hydraulic fluids, and have largely superseded mineral oils in this application. Some tertiary phosphate esters are used as anti-wear additives, and primary and secondary types as anti-oxidants and rust inhibitors.

TABLE VI
Properties of a Mixture of Hindered Esters

Viscosity, cSt	
at −40°C	7800
at −18°C	800
at 40°C	24.1
at 100°C	4.85
Viscosity Index	126
Pour point °C	< −55
Flash point (IP 36)°C	257
Density at 20°C	0.985

Silicate esters are of interest because of their flat viscosity/temperature curves and good high-temperature properties, but their use is limited by poor hydrolytic stability. However, they have found some applications as high-temperature aircraft hydraulic fluids, as coolants in weapon electronic systems, and in specialized greases. More recently alkyl silicate esters have been developed which show improved hydrolytic stability without loss of other desirable properties.

Both diesters and polyol esters, now firmly established as aviation gas turbine lubricants, are finding increasing applications as compressor and refrigerator lubricants.

Halogenated hydrocarbons

Although many halogenated hydrocarbons have marked toxicity, and products such as polychlorinated biphenyls (PCBs) are no longer in general use because of their environmental impact, there are some 'oily' fluids of this class which do not present a particular hazard because of their low volatility. Chlorinated aliphatic paraffins and chlorinated paraffin waxes are commercially available examples of products used extensively in cutting fluids owing to the chemical reactivity of the halogen atoms.

The chlorofluorocarbons, which are polymers of hydrocarbons in which all the hydrogen atoms have been substituted by the halogens, are very inert chemically and thermally very stable. These compounds have been used in specialized lubrication applications, for instance in oxygen compressors.

Polyphenyl ethers

Polyphenyl ethers such as *m*-bis (*m*-phenoxy phenoxy) benzene, though they have poor low-temperature properties, moderate viscosity/temperature characteristics and poor lubricity, are extremely stable thermally and have been used for appreciable periods at temperatures as high as 500 °C. They are also unusually resistant to nuclear radiation and have been considered for use in advanced aircraft gas-turbine lubricants and as high-temperature hydraulic fluids in rockets and other space vehicles.

Polyalpha olefins

The polyalpha olefins are a relatively new class of lubricants produced by oligomerization of linear alpha olefins, the main feedstock for which is ethylene. They can be manufactured in different chain and pendant alkyl group lengths and viscosities, and are finding increasing application in many lubricants as total or partial substitutes for mineral oil base stocks where certain of their inherent advantages can be exploited.

PHYSICAL AND PHYSICO-CHEMICAL PROPERTIES OF LUBRICATING OILS

Viscosity

This is the most important single physical property of a lubricant because it largely determines the oil's ability to lubricate.

Viscosity is a measure of the resistance to flow of liquid under an applied pressure gradient and its value is given by the ratio of the applied shear stress to the rate of shear.

$$\eta = \frac{P(\mathrm{d}r)}{A(\mathrm{d}v)}$$

Where η is the viscosity, P is the shear force applied to a plane of area A, r is the distance of the plane from a stationary wall, and v is the velocity of the plane in a direction parallel to the stationary surface. When these parameters had

unit cgs values the viscosity unit was the poise and the viscosity is the 'dynamic viscosity'.

When the dynamic viscosity is divided by the density of the liquid at the same temperature the result is termed the 'kinematic viscosity', the unit of which was the stokes. This is of value because kinematic units are relevant to many flow phenomena calculations and viscosity measuring devices. Since both of these fundamental units are large in relation to the viscosity of many common liquids, it was usual to employ units of one hundredth their value termed centipoise (cP) and centistokes (cSt) respectively. The official SI (Système International d'Unités) unit for dynamic viscosity is Ns/m^2 or Newton second per square metre, and for kinematic viscosity m^2/s or metre squared per second, with the recommended units of more convenient size one-thousandth of these values, i.e., mNs/m^2 and mm^2/s as alternatives to cP and cSt. However, the latter are still customarily used in the oil industry.

It is customary to measure most lubricant viscosities in kinematic units, and this is most accurately done in U-tube capillary viscometers of the Ostwald type. The modification of Fenske, Fitzsimmons, and Ubbelohde are commonly used, while the Houillon variant is useful for small samples. The principle involved is to time the flow of oil at a constant temperature through a calibrated capillary and to convert the time to kinematic viscosity by the use of factors determined for the individual viscometers.

Whilst there are still references made to viscosities in terms of earlier empirical units of no real physical significance, these are now largely obsolete, except in terminology terms. For example, it is still common practice to refer to 150 and 500 solvent neutrals which relate to the obsolete Saybolt viscosity measured at 100°F and originally used extensively in the United States. These units arose with early types of efflux viscometers where the time of flow in seconds of a given volume of oil at a constant temperature through a standard orifice was measured. In Britain the Redwood viscometer was used whilst on the Continent of Europe the Engler viscometer was the preferred instrument. Using this instrument it was usual to express viscosities in Engler degrees derived from the ratio of the observed flow time at each temperature to the efflux time of an equal volume of water at 20°C.

These instruments are now very rarely used and any viscosity figures that are quoted in these obsolete terms are invariably derived by conversion from directly determined kinematic viscosity values. Conversion can also be effected between one set of viscosity units and another by empirical formulae, prepared tables or charts of the nomogram type.

The American Society of Automotive Engineers introduced, many years ago, two arbitrary systems of classification for automotive crankcase and gear oils respectively. SAE numbers were given to families of oils falling within prescribed viscosity limits at specified temperatures. Oils qualifying for one SAE number under the crankcase oil classification could also qualify for an entirely different SAE number within the gear oil classification.

Both classifications have seen changes since the introduction of the scheme, but particularly so the crankcase oil classification. The latest classification, SAE J300e, comprising multi-temperature cold cranking simulation (CCS) and mini-rotary viscometry (MRV) was made mandatory in March 1982. The high temperature viscosity measurements remain the same as for the previous

J300d classification, but changes were made to the low temperature 'W' viscosity aspects. J300e also widened the classification by introducing new ratings at either end of the spectrum. These are SAE 0W and 25W grades designed to reflect more accurately engine oil operation under extreme climatic conditions and to provide a more global coverage. The principal motivations for the introduction of the new J300e classification were twofold. First, many engine failures due to the inability of an oil to be pumped at low temperatures had been experienced. J300d predicted low temperature viscosity in the CCS at high shear rate only. There was no measurement of low shear behaviour to predict the ability of an oil to flow through the oil screen to the pump inlet at low temperatures. Secondly, it was felt more appropriate to determine viscosity at those temperatures at which the lubricant was designed to operate. Table VII shows the SAE J300e classification for crankcase oils, although it is

TABLE VII
SAE Viscosity Grades for Engine Oils—J300e

SAE viscosity grade	Viscosity[a] (cP) at temperature (°C) Max	Borderline pumping temperature[b] (°C) Max	Viscosity[c] (cSt) at 100°C Min	Max
0W	3 250 at 0.30	35	3.8	—
5W	3 500 at 0.25	30	3.8	—
10W	3 500 at 0.20	25	4.1	—
15W	3 500 at 0.15	20	5.6	—
20W	4 500 at 0.10	15	5.6	—
25W	6 000 at 0.5	10	9.3	—
20			5.6	Less than 9.3
30			9.3	Less than 12.5
40			12.5	Less than 16.3
50			16.3	Less than 21.9

[a] ASTM D2602—modified.
[b] ASTM D3829.
[c] ASTM D445.
Note 1 cP = 1 mPa·s; 1 cSt = 1 mm^2/s.

expected that a stable pour-point test will be introduced for the SAE 0W, 5W, and 10W oils as an additional test to counter gelling problems due to a phenomenon known as pour-point reversion. Table VIII gives the corresponding classification for transmission and axle oils.

In that part of Table VII covering the 'W' oils (the 'winter' grades) there are now two requirements. Firstly, CCS measurement of high shear viscosity to predict film strength in bearings, piston ring zone, and valve gear. J300e classifies oils by a maximum viscosity at a temperature relevant to each 'W' grade in contrast to J300d where classification was made at a fixed temperature of −18°C. The second requirement is MRV measurement of low shear rate viscosity to predict oil pumpability at low temperatures. The MRV classifies oils by the maximum temperature at which a fixed viscosity is reached. This temperature is known as the Borderline Pumping Temperature (BPT) and can be simply defined as 'the lowest temperature at which an oil can be

TABLE VIII

SAE Viscosity Classification for Axle and Manual Transmission Lubricants

SAE viscosity grade	Maximum temperature for viscosity of 150 000 cP[a] °C	Viscosity at 100°C[b] cSt Minimum	Maximum
70W	−55[c]	4.1	—
75W	−40	4.1	—
80W	−26	7.0	—
85W	−12	11.0	—
90	—	13.5	<24.0
140	—	24.0	<41.0
250	—	41.0	—

[a] Centipoise (cP) is the customary absolute viscosity unit and is numerically equal to the corresponding SI unit of millipascal-second (mPa.s).

[b] Centistokes (cSt) is the customary kinematic viscosity unit and is numerically equal to the corresponding SI unit of square millimetre per second (mm^2/s).

[c] The precision of ASTM Method D2983 has not been established for determinations made at temperatures below −40°C; consequently, this fact should be realized in any producer consumer relationship. It is expected that ASTM will shortly undertake work in the range down to −55°C for D2983.

continuously and adequately supplied to the oil pump inlet of an engine' such that adequate oil pressure during the starting/warm-up period is maintained.

Under the new classification monograde 30 and 40 products can become multigrade 20W/30 and 25W/40 respectively but such blends are not in the spirit of multigrades which should still possess adequate viscosity/temperature characteristics either naturally or through the use of additives. Furthermore, it is possible for an oil to satisfy the requirements of more than one 'W' grade and in such instances the lowest 'W' grade satisfied should be referred to. Thus an oil meeting the requirements for SAE grades 10W, 15W, 20W, 25W, and 30 should be referred to as an SAE 10W–30 grade only. SAE viscosity grades do not relate to performance standards which are often identified by the API service classifications, the CCMC European sequences, and military specifications.

It will have been obvious from the viscosity figures already quoted for several liquids that there is a marked change of viscosity with change of temperature at a rate which differs according to the type of liquid. The most widely used way of characterizing this effect for any liquid is the 'viscosity index' (VI), an empirical concept based on the behaviour of mineral oils proposed by Dean and Davis.

In this system, Pennsylvanian (paraffinic) oils of a selected type which show a desirable, relatively small change of viscosity with change in temperature, were given a VI of 100, while selected Coastal oils showing less desirable viscosity/temperature characteristics were given a VI of 0.

Tables are available for the rapid indication of the values of the VI of an oil from determined viscosity in cSt at 40°C and 100°C. Should these tables not be available, VIs can be calculated from the formulae given in IP Standard Method 226.

There have been many systems proposed for the numerical expression of the

viscosity/temperature relationship and among these may be mentioned the Hardiman and Nissan 'Rational Viscosity Index', the Waterman index given by the logarithm of the ratio of the kinematic viscosity at 20°C to that at 70°C, and the Walther 'Pole Height' which achieved some popularity on the Continent of Europe. The latter is based on the fact that a plot of log (viscosity in cSt plus a constant) against log absolute temperature is linear for most mineral oils and for many other liquids, and that the viscosity lines of oils can be arranged in groups, each converging on a single point which characterizes that group. The height of each point or 'pole' above the base line is used for this purpose. However, the Dean and Davis type viscosity index system is likely to remain the most popular internationally.

An understanding of viscosity effects depends on the appreciation of kinetic effects in liquids. Viewed in its simplest terms it is easy to visualize more freedom of action for small, spatially compact molecules than for those which are large and gangling, provided the 'rigidities' of the molecular structures are similar. Thus, hydrocarbons of a given type will have higher viscosities at a given temperature as their molecular weight increases.

However, for a given molecular weight, branched-chain hydrocarbons which, though compact, are flexible, allow adjacent molecules in the liquid to slide past one another under a relatively low applied shear stress, whereas linear compounds are more viscous, and ring compounds, which are relatively rigid, more viscous still. Viscosity index behaviour can similarly be related to the hydrocarbon molecular structure of the components of the liquid, as can the different viscosity behaviour under various rates of shear which can distinguish Newtonian or simple liquids from non-Newtonian or complex liquids.

Of the latter, where viscosity varies with rate of shear, the commonest examples are solutions of high molecular weight polymers such as are used for improving the VI characteristics of oil blends. Two-phase colloidal solid/liquid and liquid/liquid systems will also show this anomalous viscosity behaviour.

Additives used as VI improvers include oil-soluble olefin polymers of average molecular weight in the region of 20 000, methacrylate fatty alcohol/lower alcohol ester copolymers in the range of 20 000 to 250 000, alkyl styrene polymers in the region of 50 000 and vinyl acetate/fumarate fatty alcohol ester copolymers in the region of 100 000. All these materials thus have molecular weights many times greater than the average molecular weight of the liquids in which they are dissolved.

Small concentrations of such polymers increase the viscosity of an oil blend over the whole operating temperature range, but the increase is proportionally higher at high temperature than at low. The consequent improvement in VI is not linearly proportional to concentration. A marked improvement is provided with quite a small addition, successive additions having less and less effect. Thus, the economic dosage for each polymer type rarely exceeds a few per cent.

For oils of a given initial viscosity index, greater VI improvement is given with low viscosity than with high viscosity oils, although the actual viscosity increase will be larger with the latter. This VI effect is largely a fortuitous result of the VI system. However, in oils of the same viscosity but of different initial VI, a greater VI increment is provided with oils of initially low VI than with high VI oils. This effect is related to the structure of the hydrocarbons in the oil and that of the additive. It must not be thought that a poor quality oil can be

effectively turned into a good quality oil by this means, and generally the most economic use of VI improver results when a base oil of high VI is employed. Nor must VI be confused with quality or performance, but used solely as a guide to viscosity/temperature relationships.

Mention has been made of the variation in the viscosities of polymer solutions with various rates of shear. The loss of VI at high rates of shear will be partly of a temporary nature and partly permanent. The former is due to the long-chain polymer molecules orientating themselves in the direction of flow, while the latter is usually explained by the disruption of the polymer molecules into fragments of lower molecular weight and VI improving properties. While VI improving additives are closely controlled in manufacturing to minimize this latter effect, it cannot be eliminated entirely, so that first the suitability of a composition containing such polymers will be dictated by the shear conditions existing in the application, and secondly some VI deterioration must be expected in service to a degree which increases with the polymer concentration and varies in amount with the polymer type.

There is a very close relationship between temperature/viscosity and pressure/viscosity behaviour of oils which can be explained theoretically from a consideration of the spatial configuration of the molecules and the forces between them. Thus, although all liquids will show an increase in viscosity with increase in pressure, the effect is least with oils of high VI, as shown by the ratio of the viscosity at 700 bar (Vis_p) to that at atmospheric pressure (Vis_o) at similar temperatures appearing in Table IX. Although they are no longer used, values for sperm oil and chlorinated diphenyl have been included for comparative purposes.

Although, as has been remarked, a polymer dissolved in a low viscosity liquid will increase the viscosity over the whole temperature range, the pressure/viscosity coefficient of the blend will be dominated by that of the low-viscosity component.

The viscosity behaviour of a lubricant is of importance because of its implications in hydrodynamic or fluid-film lubrication for which designers of machinery aim as often as possible. The separation of metal surfaces under motion by a finite fluid film will result in the lowest friction and thus the highest efficiency. The establishment of the fluid film may be by hydrostatic means or, more commonly, as a result of the moving part dragging the lubricant into the loaded zone through a converging clearance. In both methods a pressure is built up in the fluid film to a degree that floats the moving surface away from the stationary load-carrying surface.

The complexity of the equipment required for the hydrostatic system has limited its application to only a few items of machinery, the best example being

TABLE IX

Approximate Pressure/Viscosity Behaviour at 700 bar and 40° C

Oil	Sperm	Castor	Paraffinic	Mid-continent	Naphthenic	Chlorinated diphenyl
Vis_p/Vis_o	1.5	3.0	3.6	5.4	7.6	19.0
VI	180	90	100	70	0	−70

provided by the 'jacking' system used on some large steam turbine machinery to float initially the heavy rotating member when running up to speed.

The most common application of the hydrodynamic lubrication principle is in the sleeve bearing and journal. In this the running clearance, coupled with the eccentric attitude adopted by the shaft, automatically provides a converging clearing which varies with the applied load and speed conditions.

It has been customary in sleeve bearing design to employ the Sommerfeld relationship for bearing friction:

$$S = \left(\frac{\mathcal{Z}N}{P}\right)\left(\frac{r}{C}\right)^2$$

where S is the Sommerfeld number, a dimensionless number characterizing hydrodynamic operating conditions, $\mathcal{Z}$ is the viscosity of the lubricant, N the journal speed, P the load, C the clearance and r the journal radius. Since the square term is constant for any bearing, and fairly constant at about 500 for most bearing designs, it is usual to aim at a low value of the other term by selecting the oil viscosity to correspond to the applied load and speed conditions. The limiting value is between 5 and 10 when the units are centistokes, rev/min, and lb wt.

Some, but insufficient, attention has been paid to the influence of temperature and pressure distribution within the bearing on the viscosity of the lubricant film. The pressure effect would suggest that lower viscosity oils can be used for sleeve bearing lubrication than the conventional approach would predict, and this would provide lower power loss and temperature rise. The temperature rise within the oil film would suggest that oils of high VI will permit higher loads to be carried in a given journal design than will oils of low VI. With those oils containing VI-improving polymers it is not so certain that the latter advantage is provided to the degree that normally determined viscosities might indicate because of the shear instability of some of the polymers.

Considerable interest has been shown in recent years in lubrication conditions, such as those sometimes obtaining in gears and rolling contact bearings, in which the pressures are very high, so that while it is possible for a hydrodynamically generated oil film to be formed between the surfaces by an essentially wedge mechanism, the classical theory must be modified to take into account the elastic deformation of the surfaces due to the high pressure, and the increase in the viscosity of the oil with pressure. In this regime of elastohydrodynamic lubrication, the film thickness is only slightly dependent on load, and is much less than those normally obtained in, for instance, plain journal bearings. Such systems are, therefore, more sensitive to surface roughness.

Vapour Pressure

Under equilibrium conditions the atmosphere above a liquid will hold a concentration of vapour from the liquid and this is controlled by the pressure and temperature conditions prevailing. It is usual to express this concentration in terms of the pressure the vapour would exert if it alone filled the atmospheric space in the container. If conditions are imposed which prevent the attainment

of equilibrium, for example the continual sweeping away of the vapour, then evaporation of the liquid will occur, while if the applied pressure equals the vapour pressure at any given temperature the liquid will boil.

Since the volatility of liquids used as lubricants should be low to avoid excessive consumption and the development of dangerous or harmful vapour concentrations, their vapour pressure at normal temperatures is usually very low. This means that their boiling points at atmospheric pressure are high, and usually high enough to produce degradation if distillation is attempted. Thus, distillation at reduced pressure is nearly always employed, although the exploitation of methods which in effect are similar to distillation at reduced pressure is also resorted to as in the steam distillation technique.

There is an obvious but very good connection between molecular weight, vapour pressure, and viscosity in systems of hydrocarbons of similar chemical type and structure. A low molecular weight usually implies high vapour pressure and low viscosity because of the mobility of the molecules, and a high molecular weight makes for low vapour pressure and high viscosity.

Thus, arranging lubricating oils in order of increasing viscosity roughly places them in order of decreasing vapour pressure at a specified temperature. This is only approximate because most lubricants are not pure compounds but complex mixtures.

The vapour pressure of a mixture is given by the sum of the partial pressures of the components, each contributing in proportion to its molecular fraction of the mixture, provided no odd vapour solubility effects occur with the components.

When the components are chemically similar, as for petroleum lubricating oils, interaction does not arise, but for chemically dissimilar materials odd solubility features are quite common and anomalous vapour pressure behaviour then occurs.

Vapour pressures can be measured by determining boiling points at reduced pressures and extrapolating the results to the temperature region in which interest centres. This method gives only very approximate results because lubricants are usually of fairly wide boiling range and it is difficult to decide when 'boiling' really commences. A more accurate method involves weighing the fractions carried over by a known volume of inert gas at the temperature and pressure conditions of the test. Other physical methods have been proposed from time to time and it is now recognized that, at least for lower molecular weight petroleum fractions, vapour pressure can be calculated with reasonable accuracy from gas–liquid chromatographic data.

The vapour pressure of lubricants is probably of greatest significance when they are to be used in vacuum pumps, for the lowest pressure obtainable will be the vapour pressure of the lubricant at the temperature of pump operation. Most standard lubricants are unsuitable for use at the lowest pressures and close-cut 'molecularly distilled' oils or synthetic lubricants are then used.

With those liquids giving flammable vapours there will obviously be some correlation between vapour pressure characteristics and flash point behaviour. Lederer has remarked that for petroleum hydrocarbons, the vapour pressure is about 10 torr at the flash point temperature, but this is only a very approximate relationship and cannot be extended to fluids of even only slightly different chemical compositions.

Flash point determination consists of heating a given volume of liquid at a standard rate of temperature rise until vapour is produced to such a degree as to give a flammable mixture with air in an enclosed space (i.e., closed flash point temperature) or with air in an open cup (i.e., the higher open flash point temperature), ignition resulting from the application of a small flame. At a higher temperature still, known as the fire point, not only will the vapour/air mixture 'flash', but the liquid will continue to burn. With lubricating oils at their flash point temperatures, some degradation of the hydrocarbon molecules is beginning to occur so that the correlation of flash point with vapour pressure characteristics cannot be exact.

The vapour pressure or volatility characteristics of IC engine lubricants have been invoked as among the factors influencing oil consumption, and oils having high flash points and relatively narrow boiling ranges are, therefore, considered desirable for this duty.

Thermal Properties and Effects

The important influence of temperatures on the physical and chemical behaviour of lubricants is discussed in other sections, but some mention of other effects which occur at high and low temperatures is essential. Although these have been grouped in this section for convenience, this in no way implies that they can necessarily be dissociated from other temperature-dependent effects.

Cracking

This is particularly illustrated by the thermal degradation or 'cracking' of lubricant hydrocarbons into fragments of smaller molecular weight, including the ultimate fragment, carbon, which is nearly always associated with this process in the form of amorphous deposits. Under inert atmospheric conditions this process can be followed clearly and even quantitatively in some cases, as illustrated, for example, by the commercially important refinery cracking processes forming the first stage in the conversion of high molecular weight stocks into high-octane gasoline.

However, in most lubricant applications involving high temperatures where no attempt is made to exclude atmospheric oxygen, oxidative scission of the lubricant hydrocarbons will also occur. Aldehydic and acidic derivatives are produced which may, like the products of all cracking processes, be revealed by their pronounced depression of the flash point of the lubricant.

The rate of cracking increases rapidly with rise in temperature and the susceptibility to cracking with rise in molecular weight; saturated hydrocarbons are less stable than aromatics and branched-chain paraffins less stable than straight-chain hydrocarbons. The depolymerization of some polymers at high temperatures is an analogous process.

Cracking is catalysed by a variety of materials. In manufacturing processes activated filter clay can, under some conditions, accelerate cracking and lead to quite high product losses. The transition elements cobalt, nickel, and even iron also exhibit a powerful effect, while aluminium halides are also notable because

of their possible production in gasoline engines from the reaction of light alloy components with degraded lead scavengers.

Peroxide formation has been shown to be the rate-determining factor in oxidative cracking and depolymerization, and additives capable of limiting the formation of peroxides will successfully inhibit this mode of degradation. Thermal cracking does not lend itself to inhibition, although the stifling of catalysts is a real possibility; indeed, the carbon deposits formed in cracking processes may effectively isolate catalytic influences and result in a lower cracking rate.

Whatever beneficial effects carbon deposits may confer in this direction, they are obviously very undesirable in sensitive high-speed machinery and 'coking' test methods are employed to estimate in the laboratory the carbon-forming tendencies of lubricants. The Conradson and Ramsbottom methods are essentially similar, differing only in the type of apparatus employed, and consist of heating a sample of oil in a loosely closed container at a controlled high temperature. Evaporation of the sample occurs through distillation and cracking, and the carbonaceous residue is weighed.

These tests were originally devised for the examination of the carbon-forming characteristics of lubricants under the high temperature conditions existing in steam engines and are best suited to interpretation in this way. They have often been applied to the investigation of carbon-forming tendencies of oils used in entirely different high temperature conditions, as occur, for example, in IC engines, but misleading conclusions can be drawn because the oxidizing conditions existing in the practical application are absent in the test. The results of the conventional coking tests are also hardly significant when the tests are applied to modern highly additive treated oils, such as motor oils and marine engine cylinder oils, in which the metal-containing additives leave heavy residues which are not 'coke' as normally interpreted. The tests are, therefore, more usually restricted to straight mineral oils and oils containing only ashless additives.

It has been stated, as a result of observations from coking tests, that paraffinic oils give a hard compact form of carbon deposit, while the naphthenic oils produce fluffy soft deposits, so that the latter oils appeared more suitable for IC engine lubricants. Whilst this may have been true in the past, the difference is not very marked in most IC engine applications, and high VI paraffinic oils are very widely used. Similarly, it was considered that in marine diesel engines, reduced exhaust deposits would be obtained with naphthenic, medium to high VI oils, as compared with paraffinic oils, owing to the greater ease with which the friable 'coke' deposits given by the former were broken up and dislodged. However, there has been a trend towards the use of paraffinic oils for virtually all marine applications over the past eight years or so, modern formulatory technology having more than compensated for the 'friable carbon' virtues of naphthenic oils. Indeed, nowadays the performance demands of modern, very highly rated piston engines could not be so adequately met by naphthenic base oils.

The coke deposit is largely derived from high molecular weight 'petroleum resins' of complex structure. The concentration of these components varies with the source of the crude and the degree of refining; thus coking tests are most valuable for following these features. The tests have also been applied to

laboratory oxidized oils to examine the effect on carbon-forming tendencies of polymerized oxidation products.

Pour point

At low temperatures the normal increase in viscosity which follows falling temperature can, with petroleum products, be considerably enhanced if a solid crystal phase begins to appear. Such an effect is most commonly due to the separation of wax-like normal paraffins, the crystals of which grow, interlock, and form a matrix to restrict the fluidity of the still liquid components. The pour point is the lowest temperature at which a lubricant will still flow by gravity under prescribed conditions, and with undewaxed oils can occur at temperatures well above the freezing point of water.

The most widely used methods for dewaxing lubricating oils involve the use of a solvent, or a mixture of solvents one of which has preferential solubility for the oil phase rather than the wax, chilling the solution and filtering off the wax that separates. Propane is one such single solvent, while typical solvent pairs include butanone/toluene, liquid SO_2/benzene, and dichloroethane/dichloromethane, and the process normally yields oils of pour point approximating to the filtration temperature. Direct chilling of oil and separation of precipitated wax by filtration is still practised, but is limited in scope by the high viscosity of the oil at low temperature and rarely produces material of lower than about $+3°C$ pour point. However, for most purposes, oil is dewaxed by a solvent method to a pour point of $-9/-15°C$ and a final lower pour point achieved by additive treatment.

Pour-point depressing additives do not prevent the crystallization of the wax solids, but inhibit crystal growth by coating the micro crystals as they form; it has been suggested that these additives may also prevent adsorption of the molecules of the still liquid components, a process which has been advanced to explain certain aspects of lubricant behaviour at the pour point. The additives are commonly of two general types, aromatic-paraffin wax condensation products, and alkyl methacrylate polymers, which also function as VI improvers, but certain vinyl ester and alkylated polystyrenes have also been proposed.

Pour-point depressants are not often used in high viscosity lubricants because the low-temperature viscosities of these oils are too high for most practical applications. The presence of a pour-point depressant in a lubricant can be detected by comparing the pour point and the cloud point (the temperature at which solids begin to separate); in the absence of the additive the two temperatures are almost coincident, while they diverge as the concentration of the additive increases up to a maximum temperature difference beyond which further additive addition makes no contribution. This critical concentration for optimum effect is controlled by both the oil type and the additive composition. Another method of detection, if the only additive suspected is a high molecular weight pour-point depressant, is separation by dialysis through a rubber membrane, using n-hexane as an extraction medium for the oil. The dialysis residue from a fully additive treated oil will, however, usually include any VI improver (which can itself often act as a pour-point depressant), ashless dispersant and metallic detergent present.

Specific heat

Quite often in lubricant applications it is essential to establish optimum conditions for the transfer of heat and, indeed, the cooling function of lubricants in such applications as sleeve bearings, IC engine pistons, and high-speed gearing is a vital auxiliary feature.

A knowledge of the specific heats of lubricants is thus of considerable value in estimating the likely rise in temperature for a given set of heat transfer conditions. Without exception, the common liquids used as lubricants have specific heats lower than that of water as the approximate values in Table X illustrate.

TABLE X
Specific Heat of Lubricants

	Specific heat at 20°C kJ/kg°C
Polyhydric alcohols	2.43
Petroleum oils	1.88
Silicones	1.47

The specific heat of a liquid lubricant increases with temperature and in the case of mineral oils is a function of density (or of average hydrocarbon type). For these oils the specific heat, C_p, may be calculated fairly accurately at any temperature from the following expression:

$$C_p = (1.69 + 0.0034t)d^{-1/2}$$

where t = temperature in °C and d = density of oil at 20°C.

Thermal conductivity

In many heat transfer problems where bulk quantities of oil are involved, viscosity has a decided influence over the establishment of convection current or volume flows if forced circulation is employed. Under thin film conditions, as exist, for example, between piston rings and the piston or cylinder wall, the thermal conductivity of the oil is significant. Most lubricants have quite low conductivity and a few approximate values for typical lubricants are given in Table XI.

The thermal conductivities of liquid lubricants fall with rise in temperature, and for mineral oils are again a function of density. For the latter oils the

TABLE XI
Thermal Conductivity of Lubricants

	W/m°C
Polyhydric alcohols	0.25
Aliphatic esters and fatty oils	0.168
Mineral oils	0.126
Silicones	0.118

conductivity λ at any temperature can be approximated from the following formula:

$$\lambda = 0.117(1 - 0.0054t)d^{-1}$$

where λ is expressed in W/m°C.

Density

The densities of all lubricants alter with change in temperature and this is of importance in numerous ways. To name a few, this behaviour must be known for: conversion of kinematic to dynamic viscosity units; the calculation of centrifugal pump performance; and calculations relating to hydrokinetic energy transmission devices.

Fortunately the density/temperature behaviour of mineral oils can be calculated quite easily from the empirical equation:

$$d_t = d_{20\,°C} - A_1(t - 20) - A_2(t - 20)^2$$

The coefficient A_1 was thought at one time to depend approximately on the density of the oil and some density tables have been based on this assumption. However, it is now clear that quite accurate density calculations can result from the use of the true coefficients A_1 and A_2, which are functions of the average molecular weight of the hydrocarbons in the oil (the molecular weight is itself obtainable by fairly simple empirical methods). Typical values of the coefficients are given in Table XII.

TABLE XII
Density/Temperature Coefficients

Molecular weight	$A_1 \times 10^5$	$A_2 \times 10^7$
300	67	0.8
350	65	1.3
400	63.6	1.7

The data in Table XIII for a paraffinic brightstock are given to indicate the order of difference between conventional and true coefficients.

There is obviously a direct relationship between the coefficients of expansion of a lubricant and its density variation with temperature. The one is, therefore, easily calculated from the other.

TABLE XIII
Conventional versus True Density/Temperature Coefficients

Molecular weight	$d_{20\,°C}$	A_1 (conv.)	A_1 (true)
800	0.875	0.000 65	0.000 59

Electrical Properties

Elsewhere in this book the electrical properties of insulating and transformer oils are discussed. Similar properties will be exhibited by lubricating oils, except that some additives and most common contaminants will exert a profound influence on their electrical behaviour.

The electrical properties of lubricating oils can be of considerable practical significance as has been stressed by T. Salomon. The development of electrostatic charges in machinery insulated from an earth by the lubricant films within the machinery has been clearly established. The best-known example is in steam turbines, where the passage of damp steam across the rotor blades can develop very high electrostatic potentials. Similar effects have been observed in IC engines, air compressors, and other machinery where a dielectric is in rubbing contact with an insulated system.

When electrical discharge takes place through an oil film, some observable changes in the solid surfaces, particularly the earthed surface, can be expected. For example, the typical hemispherical pitting which can occur with electrical discharge in anti-friction bearings is well known. Salomon has collected evidence in support of the view that many changes in lubricating oil qualities, some deposit formation, wear, and distress in bearing and gear operating surfaces are of electrical origin. Much still remains to be done in this rather neglected sphere of lubrication technology.

Another sphere which has been rather neglected but which may also be of considerable practical significance, is the electrochemistry of lubricating oils.

When mineral, vegetable, and animal oils are subjected to silent electric discharge in thin films, polymerization and molecular rearrangement occurs, and products of greatly increased viscosity result. This is the basis for the 'Voltol' or 'Elektrion' process, the products of which were claimed to improve the viscosity, dispersancy and oiliness characteristics of mineral oils and have been used as additives in some lubricating oils.

When high alternating stresses are applied to mineral oils, resulting in partial discharge, gas is evolved, the gas consisting mainly of hydrogen and methane. The volume of gas produced depends on the hydrocarbon types in the oil and on any additives present, but is otherwise roughly proportional to the power input. When the stress is sufficiently high to strike an arc, gas evolution can be more copious, with hydrogen and acetylene as its main constituents. In fact, analysis of gases extracted from oil in transformers is used as a basis for the diagnosis of faults in the transformers, though in this special application the constitution of the gas is also greatly influenced by electrical effects on organic insulating materials in the transformers and by local overheating effects on oil and insulation.

Not insignificant potentials have been measured between electrodes of common bearing metals immersed in oxidized lubricating oils, but the importance of this in relation to bearing corrosion problems has not been clearly established. In experimental work, electromotive forces of the order of 1 volt have been measured between dissimilar metals separated by oil containing detergent additives, but none where the oil has been a non-polar petroleum fraction.

Properties Under High Pressure

In most uses of lubricating and hydraulic oils involving application of pressures up to about 30 bar, the liquids may be considered incompressible, although in fact a negligibly small compression is involved. Compressibility may be defined as the reduction in volume of a fluid when pressure is applied, and can be expressed as

$$C = \frac{1}{V_0}\left(\frac{dv}{dp}\right)$$

where C is the compressibility, V_0 is the initial volume, and dv/dp is the rate of change of volume with pressure.

At very high pressures the total volume decrease due to compressibility may be very significant, and may be complicated if a solid phase separates or a change of state occurs, because solidification is most commonly marked by a significant volume decrease.

Most lubricating oils if well dewaxed will not exhibit phase separation until extremely high pressures are reached (3000–5000 bar) and gradually decreasing compressibility is, therefore, exhibited over a wide pressure range. The average compressibility of lubricating oils in the pressure range 1–1000 bar at 40°C falls between 4.5 and 5.0 × 10^{-5} according to data published by Dow and Fink.

The compressibility of mineral oils is slightly greater than that of water and varies, though only to a small extent, with oil type. Aromatic oils tend to be least compressible and naphthenic oils most, with paraffinic oils in between. Compressibility increases with rising temperature, while for oils of similar type, those of higher viscosity are slightly less compressible than those of lower viscosity. For instance, for a paraffinic oil with a viscosity of 34 cSt, an applied pressure of 3300 bar caused a volume decrease of 12.4 per cent, while oil from the same crude with a viscosity of 320 cSt exhibited a volume fall under the same pressure of 11.9 per cent. Table XIV shows typical volume changes for a light lubricating oil, at 40°C, under pressures up to 1000 bar.

TABLE XIV
Compressibility of a Lubricating Oil

Pressure (bar)	Relative volume
0	1.0
100	0.993
200	0.987
300	0.981
400	0.975
500	0.968
600	0.962
700	0.956
800	0.950
900	0.944
1 000	0.938

With the compression of matter into a small volume, an increase in density occurs which is readily calculable from the compressibility. As the molecules are driven closer together under the effect of pressure an increase in viscosity is another consequence on which appropriate comments have already been made. Since paraffinic oils have lower compressibility than naphthenic oils, and fatty oils usually have compressibilities lower than either, the viscosity increase with pressure is least with fatty oils and greatest with naphthenic oils.

The latter point has sometimes been invoked as one factor to explain the better lubricating ability of fatty oils, but this is open to considerable doubt, for liquids of both much lower and much higher compressibility are rather inferior to mineral oils as lubricants. For example, glycols have compressibilities only about half that of mineral oils, and silicones are about three times as compressible at normal temperatures.

Compressibility is of most practical importance in hydraulic applications. However, the yield of the metals in the containing system will have the effect of increasing the absolute compressibility of the fluid to an apparent compressibility, the value of which will depend on the nature of the circuit. The engineering figure generally recommended for design purposes is 0.5 per cent per 70 bar, but this is obviously only a convenient approximation. Engineering calculations relating to hydraulic systems are often based on the reciprocal of compressibility, the bulk modulus, usually denoted K. The higher the bulk modulus, the less elastic, i.e. the 'stiffer' the fluid.

Surface Properties

The attraction existing between molecules has a net effect observable at surfaces where the existing forces are directed towards the densest concentration of matter. A direct result of this effect is the fact that liquids tend to adopt a shape of the smallest surface area, as is demonstrated in the limit by the spherical form of small droplets of liquid.

Thus an increase in the area of a liquid surface involves work done against the attractive forces and leads to an increase in the free energy of the surface. Alternatively, this may be visualized as work done against the surface tension which is the most easily determined surface property.

Since the surface tension is so closely bound up with the nature and density of packing of the molecules in the material it is to be expected that surface tension will fall with rise in temperature. This is demonstrated by the values for most highly refined, additive-free, mineral oils, which are compared with the surface tensions found in other liquids in Table XV.

When two immiscible liquid phases are in contact a new surface tension, the interfacial tension, arises at the interface, differing markedly from that of each liquid in contact with air. If a very small quantity of one fluid floats as a film on the other the resolution of the surface tensions and IFT at the film edge will show whether the film will spread across the surface or collect together in lens-like droplets. This is illustrated by data in Table XVI for a highly refined mineral oil (A) and the same mineral oil containing a small amount of dissolved free fatty acids (B) on water.

The spreading of liquids on solid surfaces, although slower, can be qualitatively understood in a similar way, but the contact angle, θ, of the liquid

TABLE XV
Surface Tension of Various Liquids

Liquid	Surface tension, mN/m or dyn/cm, approx.	
	25°C	100°C
Lubricating oils	31	24.5
Water	71.25	60
Glycerol	47.5	41.4
Triolein	27.7	23.8
Silicone	19.7	14.5

on the solid must be considered when resolving the surface forces. With most lubricating oils on clean metals, θ is very small and may, therefore, be neglected. However, the contact angle is often a useful guide to the wetting characteristics of a liquid/solid combination.

The important effect on the surface and interfacial tensions of even traces of other added materials in mineral oils is related to the tendency of these materials to concentrate in the surface layers of liquids or to be strongly adsorbed on solid surfaces. Indeed, this property of the molecules of some materials to be attracted more strongly to surfaces of other materials than to themselves is sometimes described as the forces of adhesion exceeding the forces of cohesion.

The molecules which show this particular feature are often called 'polar' because they invariably contain a polar group such as —OH, —SH, =O, =S, —CO, —COOH, $-SO_3H$, etc., attached to a long hydrocarbon chain.

The presence of surface-active materials in a lubricant must be considered jointly with viscosity when a number of important features of lubricants are studied. For example, the leakage of lubricants, when gross, is controlled almost exclusively by the viscosity, but when the volume flow is very small and dropwise the surface tension becomes of importance. Indeed, in the limit with rotary oil seals, where an oil film under the seal lip is essential to prevent heavy wear, the separation of the surfaces and the lip dimensions must be such that the surface tension of the lubricant counterbalances the forces driving the lubricant through the annular gap if leakage is to be minimized.

Surface-active agents may be included in low viscosity materials to provide penetrating oils, while different surface-active materials, usually calcium soaps, are included in non-creep oils. In the latter instance the ability of calcium soaps to provide rigid adsorbed surface films is exploited to prevent spreading and leakage.

TABLE XVI
Surface Tension, Interfacial Tension, and Spreading of Oil on Water

Combination	ST_{oil}	ST_{H_2O}	IFT	Net tension	Behaviour
Oil A on water	31	71.25	52.5	−12.25	Droplets
Oil B on water	30	71.25	34	+7.25	Spreading film

Surface tension has to be considered also in such matters as the formation of mists and the migration of lubricants from hot surfaces. The latter effect arises from the temperature-dependence of surface tension, and materials containing —OH groups, such as castor oil, show a low migration tendency.

The pronounced influence of the slightest traces of oxidation products containing carboxylic groups on the interfacial tension between lubricating oil and water has sometimes been used to follow oxidation effects in steam turbine lubricants.

Commercial additives designed to provide surface-active properties to lubricants usually contain one of the functional groups already mentioned. The most widely used materials of this type are the detergent or dispersant additives which are designed to be adsorbed on fine solid particles to prevent their coagulation, and the so-called 'oiliness' additives. These are discussed more fully below.

Phase Effects—Solids

Ideally, lubricants will give the best performance if they keep their virgin condition. Unfortunately, this state of affairs rarely applies, so that lubricant formulations must be devised which will give optimum performance under adverse conditions. One aspect of this problem is the influence that dispersed solids may have on liquid lubricants. These solids may be derived from a number of sources; for example, airborne dust, corrosion and wear products, lead compounds and soot from combustion processes in internal combustion engines, and insoluble resinous degradation products of lubricants or fuels are some of the commonest forms of solids to be found in lubricants.

Such solids are undesirable because some may promote abrasive wear if continually circulated with the lubricant, while if they settle from the liquid they may be swept into and block oilways. It is generally accepted that the particle size must be below 5 microns to avoid abrasive wear, while the rate of sedimentation under any given flow conditions will increase with the particle size and the specific gravity of the solid.

With concentrations upwards of 0.5 per cent of finely divided dispersed solid a measurable increase in viscosity may be observed, a condition which is most frequently encountered with soot-contaminated crankcase oils.

It is the purpose of detergent or dispersant additives to stabilize solid contaminants in a finely divided form, preferably below the abrasive wear size limit, and to prevent their adhesion to the lubricated surfaces. The surface-active materials finding major use are oil-soluble metal soaps of specific types and ashless polar compounds, usually nitrogenous, based on polymeric materials or having long hydrocarbon chains. Some naturally occurring oxygen and sulphur containing ingredients in the less highly refined lubricants can provide weak dispersancy properties, but their loss from the more highly refined materials is of minor importance in the presence of the much more effective dispersant additive types.

The necessity for oils of high detergency was first acutely demonstrated in high performance diesel engines, when solids resulting from thermal degradation of the fuel and lubricant led to ring sticking and undesirable piston deposits generally. The first additives employed to counteract this were metal soaps of

relatively simple type. Aluminium naphthenates, and calcium dichlorostearate, were typical materials which were subsequently discarded because of their excessive pro-oxidant properties.

The detergent additives most favoured now are the alkaline earth metal salts of petroleum or synthetic alkyl benzene sulphonic acids, preferably overbased to provide acid-neutralizing properties, the alkaline earth metal salts of alkylphenols, sulphurized alkylphenols and alkyl phenol sulphides, and the alkaline earth metal salts of long-chain hydrocarbon thiophosphonic acids. Such additives, when basic, function largely by neutralizing acidic materials and to a lesser extent by solubilizing and peptizing deposits and their precursors.

Some additives are much more active as dispersants than as detergents; they are particularly effective in maintaining solid contaminants in fine suspension, and may have little ability to remove deposits already settled on surfaces, an important function of the true detergents. The dispersants are believed to act by being physically adsorbed on the surfaces of particles of solids and thus preventing their agglomeration. They have assumed particular importance in motor oils because of the need to disperse 'low temperature sludge' in passenger cars. This is a paste-like mixture of oil, carbonaceous matter and other solid contaminants and water, this last constituent usually representing about 80 per cent, and resulting essentially from blow-by gas. Evidence has been adduced suggesting that certain nitro-nitrated lower olefins, produced as the result of the interaction of cracked fuel components with nitrogen oxides from nitrogen fixation in the combustion space, are a major cause of sludging in petrol engines. The most generally used sludge dispersing additives are the ashless, polyethylene polyamine succinimides in which the succinimide ring has a polyisobutene group, and certain nitrogen-containing methacrylate type copolymers which are also effective as VI improvers.

For many end-uses it has become necessary to include more than one type of surface-active agent to combat the different types of 'dirt' encountered in service, and mixtures of ashless and metal-containing compounds are normally employed. Considerable care is needed in formulation owing to the possibilities of interaction between different types of surface-active agent and in meeting limitations often imposed on ash levels and phosphorous contents of finished lubricants.

Attempts have been made to measure in the laboratory the relative dispersancy efficiencies of such additives. Sedimentation tests, usually using carbon black suspension, have been employed but only moderate success in correlation with field performance has resulted. This can be accounted for by the difference between most laboratory conditions and those existing in the machinery for which such lubricants are intended. In internal combustion engines deposits on hot metal surfaces must be avoided so that the dispersancy additives must have the ability of being adsorbed as readily on these hot surfaces as on the solid particles. Since water will invariably be present, this imposes another performance requirement on such additives, many of which will be quite sensitive to this factor. As an alternative method of assessing dispersant efficiency in a lubricant and for preliminary checking of dispersant and detergent additives, a 'panel coker test' is sometimes used. In this, a circulating pump splashes the heated oil under test on to metal plates maintained at various

high temperatures for fixed periods, and the assessment is based on the quantity and nature of the deposits left on the plates.

However, it is essential to submit detergent–dispersant compositions destined for use in internal combustion engines to actual engine tests under characteristic and severe operating conditions. This is obligatory with many American and British heavy duty oil specifications, where the method of test is chosen to create fairly severe ring-sticking conditions, and with specifications issued by various automobile manufacturers, in which several engine tests may occur designed to assess the high-temperature performance, the cold sludge dispersing properties and the corrosion preventive powers and many other parameters of the lubricants.

The filtration of lubricants containing detergent and dispersant additives after use in an engine may involve slightly different techniques from those employed for non-additive lubricants. Filters employing activated earth are unsuitable because the additive may be entirely removed by adsorption; some chemically treated paper filters are similarly unsuitable because of effects on the additives. Edge-type filters of compressed paper disc construction have been found to clog very quickly, and reverse flow will not clear the obstructions, producing an undesirable high pressure drop across the unit. The filters normally used for oils of high dispersancy are either those with pack elements of fairly open structure, which will pass the very fine dispersed solids, but trap the coarse dangerous solids, or those of the centrifugal type.

Oils containing dispersancy additives can be processed in industrial centrifuges, usually operated as clarifiers without a water seal. Water is not used because such oils normally show a strong emulsifying tendency with water, while the additives themselves may be water-sensitive. Water and steam washing are generally avoided for the same reasons. At one time it was common to water wash crankcase oils in low-speed marine diesel engines to reduce inorganic acidity and assist in the removal of carbonaceous matter. However, this has become unnecessary with the advent of high TBN cylinder oils which prevent the formation of acid scavenge drains, these being the source of acidic contamination through ingress into the crankcase of marine crosshead diesel engines.

The rate of sedimentation of solids from liquids depends not only on particle size, over which dispersancy additives can exert some influence, but also on the relative densities of solid and liquid, the oil viscosity, and the gravitational field. For example, high dispersancy oils are not able to maintain heavy insoluble lead compounds in suspension, and these compounds tend to deposit especially in those regions of gasoline engines where high gravitational fields are developed, for example hollow crankpins of long-throw high-speed engines.

Even the less dense dispersed solids may be removed in a reasonable time if very high gravitational fields are used. High speed laboratory centrifuges can do this, and these instruments provide a means for the rapid assessment of dispersancy. However, since many dispersancy additives provide colloidal rather than true solutions it is often found that the additive can also be removed by these instruments.

The quality of the base oil used with dispersancy additives is of no little importance. If the oil shows a high sludging tendency owing to poor refining the additive will soon be exhausted and confer no real advantage in practice.

Phase Effects—Liquids

It is generally true that two liquids of similar molecular species will be miscible with each other in all proportions, while those of markedly different chemical structure may have only limited solubility relationships, so that over a wide range of concentration two immiscible phases result.

Most of the individual lubricant types being considered in this chapter, but mineral oils especially, can be considered examples of the first class, since they invariably consist of a complex mixture of closely related isomers in stable solution which it would be commercially pointless to separate. Similarly, these mixtures may themselves be soluble in, or dissolve, closely related compounds. The most important consequence of this is the modification to the viscosity characteristics which results if the viscosity of the solute differs markedly from that of the solvent. The importance of this principle has been noted in the blending of lubricants and an extreme example is provided by the class of two-stroke engines which are reduced in viscosity with a miscible hydrocarbon to provide easy mixing with gasoline in the fuel tank of the engine. The limited solubility (about 12 per cent at 20°C) of mineral oils in castor oil is also commercially exploited to give viscosity and economic advantages in blending certain engine and worm gear lubricants, although polyglycols are now more commonly used where lubricants superior to mineral oils are demanded.

Frequently, admixture of the lubricant and a miscible fluid results by accident rather than by design. The dilution of an IC engine crankcase oil with a fuel during the operation, and especially mal-operation, of the engine is a case in point. The viscosity reduction which can result in this instance is of more practical significance than the reduction of flash point, although the latter effect is of importance in the laboratory detection of fuel dilution. Good crankcase breathing arrangements were always of assistance in controlling the undesirable consequences of contamination with a volatile fuel such as gasoline, though not very effective in respect of the heavier diesel fuels, but the modern automobile engine is, in any case, often equipped with a positive crankcase ventilation (PCV) system designed to ensure removal of blow-by gases and water vapour, besides providing the normal breathing facility. The blow-by gases are drawn, usually through a control valve, into a relatively high vacuum area such as the inlet manifold.

Sometimes undesirable lubricant viscosity reduction (or rise) is possible when leakage of lubricant from one system into another occurs, and again no simple separation of the miscible components is possible.

Water is probably the most common liquid contaminant which has only a limited solubility in most common lubricants at normal temperatures. The solubility does not vary very greatly with type for different mineral lubricating oils, and at 20°C most petroleum fractions will dissolve water to about 0.05 mole per cent (representing about 40 ppm for an average lubricating oil), the solubility increasing with rise in temperature.

At water concentrations higher than this, first a distinctive haze will be imparted to the lubricant and eventually a free water phase will appear. In enclosed crank chamber reciprocating steam engines, rotary vane air compressors and more especially in steam turbines, where heavy water contamination of the lubricant sometimes occurs, the ready separation of the water phase from

the lubricant is most essential. This property of 'demulsibility' is best obtained by the intensive refining of petroleum fractions to remove those naturally occurring polar ingredients not removed by normal refining techniques and which tend to encourage the emulsification of water into the lubricant as a dispersed phase.

Some ester type lubricants, used as fire-resistant steam turbine fluids and hydraulic fluids, are polar compounds which might have been expected to emulsify readily with water. In fact, these fluids can have quite good demulsibility, and this most probably arises from the wide density difference between these fluids and water which encourages the separation of the phases under gravitational forces.

Enhanced gravitational forces to speed up this partition in any oils having a good demulsibility are provided in centrifugal separators, which continuously remove water contamination from circulatory lubrication systems.

Solid contaminants such as dust, wear debris, rust, or soot particles will tend to collect at the oil–water interface of water-contaminated lubricants and stabilize any emulsion. Similarly, polar compounds which have a marked effect on the interfacial tension will have a powerful influence on the emulsifying tendency of the lubricant.

Materials of this type, which can occur naturally in mineral oils, are most probably long-chain unsaturated compounds, while the organic acids, or metallic soaps derived therefrom, which can result from the oxidation of lubricant hydrocarbons, sometimes account for the deterioration of the demulsibility of an oil in service.

Under those conditions where the degree of water contamination is moderate but where a corrosion or lubrication problem could result, it is usual to employ lubricants of strong emulsifying tendencies to incorporate the aqueous phase in a water-in-oil emulsion. The additives which may be intentionally added to a lubricant to achieve this are, to some extent, dictated by other properties which are also sought, but such materials as fatty oils, oil-soluble metallic soaps derived from fatty acids, or wool grease derivatives are time-honoured examples, while synthetic materials are finding increasing use.

An important property of a water-in-oil emulsion is that its viscosity is very much higher than that of either fluid component and in extreme conditions a semi-solid or grease-like product can result.

This is particularly true when a solid contaminant is also present, as commonly occurs in the crankcase of a gasoline engine under idling or cold running conditions. In this instance the fuel-rich conditions characteristic of idling can lead to a heavy load of soot in the crankcase lubricant concurrently with a high percentage of condensed water in the oil and coolant temperatures are low. If these conditions are sufficiently severe a soft sludge will settle in those parts of the engine where the lubricant flow is of low velocity. Control of such sludge by dispersants has already been mentioned, while the PCV devices usually prevent or limit such sludge formation.

Prepared water-in-oil emulsions were used with success in a number of lubrication applications, a notable example being their use as cylinder lubricants for marine diesel engines, though this is a rather special case in that the selection of such materials was based on the feasibility of introducing into the water phase soluble alkaline salts to provide rapid neutralization of acidic

products from the combustion of high-sulphur content fuels. However, problems of emulsion stability in storage could arise with such lubricants and they are now no longer marketed for marine cylinder lubrication, except for very limited usage of the van der Horst system where an emulsion is prepared immediately prior to injection.

Oil-in-water emulsions, the high water based fluids, are becoming popular for certain applications, notably hydraulic systems, where the product offers not only commercial but safety advantages.

Phase Effects—Gases

The solubility of gases in liquid lubricants expressed as the molar fraction of the mixture increases in proportion to the rise in pressure, as stated by Henry's Law and, with most gases, decreases with rise in temperature. Some departure from the ideal is usually found, the deviation varying with the nature of the gas. Much of the data which have been published on gas solubility is expressed in terms of the volume of gas, reduced to a standard temperature and pressure, which dissolves in a unit volume of liquid. Typical solubility figures expressed in these terms for some common gases in a light spindle mineral oil are given in Table XVII.

Figures published in the literature tend to show minor disagreements between observers and these are almost certainly due to differences in the experimental methods of determination.

With air and oxygen, difficulties in establishing reliable solubility data are produced by the chemical reactivity of the oxygen towards the hydrocarbon molecules, particularly in the presence of catalysts. It will be observed from the figures quoted above that the solubility of air is intermediate between those of pure oxygen and pure nitrogen; the solubility of a mixture of gases depends on the molal solubilities of each component and on their respective molal concentration in the mixture.

The rate of solution of gases is usually very much lower than the rate of evolution and both rates decrease with rise in viscosity of the lubricant. The magnitude of this effect is controlled by the conditions of exposure of the oil to the gas. The effect arises because the absorption of gas can take place only through the exposed surface area of the liquid, whereas the evolution of gas occurs throughout the body of the liquid. In the limit, the difference between the two rates is minimum for finely divided oil mists.

TABLE XVII
Solubility of Gases in Light Spindle Oil

Gas	Solubility (volume in ml of gas at 25°C, 1 bar, in 1 ml of oil)
CO_2	0.99
O_2	0.14
Air	0.11
N_2	0.09
H_2	0.05

The difference between solution and evolution rates is of significance in cavitation in bearings, in those hydraulic applications where a sudden change of cross-section in a pipeline produces a reducton in pressure and, therefore, evolution of gas, and in mass transfer effects where a lubricant flow may come in contact with gas at two different pressures.

The exposure of oil saturated with gas at a high pressure to a suddenly reduced pressure can lead to bad foaming as the gas comes out of solution, or to airlocks in hydraulic systems, for example, where pockets of gas can be trapped in bends in the pipe-work. Air can also be entrained into lubricant flows through leakage at the suction side of the circulating pump, the effect being that the air is dispersed throughout the body of the lubricant in the form of small bubbles. The rate at which the dispersed air clears from such a mixture as soon as the flow ceases is subject to much the same laws as is the sedimentation of solid particles. The rate depends on the relative density difference leading to a buoyancy effect, on the size of air bubbles, on the viscosity of the medium and on the surface tension.

Air entrainment effects have been the subject of some concern in recent years, particularly in connection with the lubrication of steam turbines, where insufficiently rapid release of gas bubbles might result in the supply of an excessively aerated oil to the bearings, and a number of tests have been devised for the assessment of oils as to their air release propensities. The finishing process in the refining of the oils can have a profound effect on this property.

In pure hydrocarbons the air bubbles reaching the surface will immediately collapse, but more commonly, especially when the lubricant cannot be considered chemically pure, stable foams can be produced. Stable foams in the lubricating medium are promoted by the presence of some material which collects at the air/liquid interface and is capable of immobilizing the liquid in the bubble walls, thus preventing the draining of the liquid from the foam. Many surface-active additives, as well as colloids, show this effect to a very pronounced degree, and the use of anti-foam additives is obligatory in many compositions containing additives of this type. However, some such additives can have a deleterious rather than a beneficial effect on the rapidity of air release, as distinct from the rapidity with which a mass of foam is broken up.

A number of anti-foam agents have been proposed, but the polysiloxanes are probably the most widely used. The concentration employed does not usually exceed 0.0005 per cent wt. The polysiloxanes are thought to act by being more powerfully attracted to the bubble surface layers than is the foam stabilizing material which is thus displaced, thereby leading to an immediate collapse of the foam. However, these materials are not sufficiently effective in some lubricating oil compositions, and certain acrylate ester co-polymers have found application, especially in hypoid gear oils. Much larger proportions than of the polysiloxanes are needed, usually of the order of 0.1/0.2 per cent wt.

Radiation Effects

The effect of silent electrical discharge (electron bombardment) on lubricating media has already been mentioned. In recent years the effects of nuclear radiations on lubricants have been extensively studied and have been shown to be somewhat similar to the electrical effects.

The feature which is common to all radiations producing significant changes in lubricants is their ability to ionize the hydrocarbon molecules in the liquid. The ionized molecules undergo a variety of chemical changes, including polymerization and oxidation, while hydrogen gas and other volatile fragments may be produced. The nuclear radiations which produce degradation are fast, slow and thermal neutrons and gamma photons. Fast neutrons collide with hydrogen nuclei in the organic molecules and eject them as protons which then cause damage by ionization of other molecules. The gamma protons are absorbed and upset the electronic system of the molecules. Electrons are ejected to produce ionization in other molecules. Thermal neutrons are captured by the nuclei of hydrogen atoms with the emission of high energy gamma rays. These produce the ionizing effects just mentioned.

Study of the rate at which degradation proceeds in terms of viscosity increase, leads to the conclusion that with most organic liquids there is a delay period in terms of total radiation dose during which only relatively minor changes occur; beyond this critical point the change in viscosity becomes most marked and the lubricant may rapidly become unserviceable. It appears that the amount of radiation damage is independent of the type of radiation involved, but is a function of the total energy absorbed by the molecules of the liquid.

It is usual to express the critical point marking the point of major change in the physical properties of the lubricant in terms of the energy dose. For most mineral lubricating oils this critical point is reached at a dosage between 1 and 5×10^8 rads. The critical point occurs at a significantly higher energy dose in those fluids containing a large proportion of aromatic hydrocarbons; this is thought to be due to the energy being absorbed as resonant energy in the aromatic ring structures.

Radiation damage can be inhibited to some extent with certain additives, but their mode of operation is not yet clearly understood. It is, however, interesting that anti-oxidation additives, which are thought to inhibit oxidation energy chains, will also function as radiation damage inhibitors.

The main requirement for radiation-resistant lubricants is in nuclear power station applications, and in the UK most of these special products have been developed to conform to specifications issued by the United Kingdom Atomic Energy Authority (UKAEA). Greases are more generally used than fluid lubricants, and these may be based on mineral lubricating oils or synthetic fluids. The properties of the mineral oils must be such as to enable the finished lubricants to satisfy many requirements in addition to radiation resistance.

Limitation of the escape of hydrocarbon molecules into the nuclear pile via the gas stream demands the use of oils with low vapour pressure and low volatility. Thermal stability is important, since the lubricants may be exposed to high temperatures in various gas environments such as CO_2, argon, helium, etc., and low volatility is of importance in this aspect, too, to avoid drying out. Accidental leakage of lubricant into the fuel ducts from such items as charge/discharge machinery and control-rod mechanisms could cause damage if the lubricant contained elements which could react with fuel-can alloy at the high temperatures of 250/500°C involved. The choice of metal-containing oil additives is limited by this consideration and by the need to avoid elements such as cadmium and mercury which have high neutron absorption capacities and which could 'poison' the reactor in the event of accidental contamination.

Preliminary evaluation of lubricants for radiation resistance can be achieved by using electron bombardment from a linear accelerator, since this has been found to give reasonable correlation with neutron and gamma-ray bombardment, but final testing is likely to be in a rig in which a closer simulation of reactor environment conditions can be provided. Irradiation is usually carried out in a spent-fuel 'cooling pond', with a gamma dose rate of 10^6 rads/h for anything from 100 to 3000 h.

Lubrication Under Boundary or Extreme Pressure Conditions

The lowest power losses in any lubricated equipment are provided when the lubricant films are very thick by comparison with the dimensional roughness of the metal surfaces involved. Under these conditions interaction between the metal surfaces is minimized and the viscosity of the lubricant is the only major factor influencing the magnitude of frictional effects, though under more extreme conditions in which, however, fluid films can still be maintained, it is the viscosity under pressure which must be taken into account; the lowest possible friction obtains if viscous drag losses are minimized.

When the load or speed conditions at the lubricated surfaces are altered so that the hydrodynamic films are less readily established, the metal surfaces will come into more intimate contact. In particular, they will first touch at isolated high spots or asperities, and welding occurs followed by breakage of the welds by shearing, thus making a major contribution to the total wear. Any interaction of the lubricant with these metal surfaces, which will usually be covered with oxide films, then becomes of very great significance. If the separation of the metal surfaces is of the same order as the surface roughness, that is, if hydrodynamic films in the load-carrying zone are only partially established or are absent, lubrication is said to occur under 'boundary' conditions. Friction is then controlled first by the nature and degree of the interaction between the lubricant and the metal surface, and any films that may be present thereon, and secondly by the physical properties of the underlying metals. If boundary conditions are brought about by high imposed loads, the oils best suited to operate in these circumstances are known as 'extreme pressure' lubricants.

Oils and additives may interact with metal surfaces in two ways, by physical adsorption, and by chemical reaction. As has been mentioned earlier, any oil-soluble materials containing polar groups will tend to collect at the oil/metal interface, with the polar group orientated towards the metal surface by which it will be adsorbed to a degree varying with the nature of the surface-active material. If a sufficient concentration of the surface-active material is present a dense adsorbed layer of orientated molecules will be produced and will effectively reduce metal to metal interaction through the lubricant film. A low coefficient of friction will result since the shear strength of the lubricant layer will be lower than that of the metals.

Long-chain fatty alcohols or acids are examples of materials which can provide benefit under boundary conditions by this mechanism, although chemical reaction of fatty acids to form layers of metal soaps is also operative and, in fact, liquid fatty acids are in general more effective as boundary lubricants than are fatty alcohols of similar chain length.

Chemical surface attack is provided by other classes of materials, notably those containing the elements phosphorus, chlorine, or sulphur. Typical examples of materials falling in each class are tritolyl phosphate, chlorinated wax, and sulphurized fatty oils; these produce, on interaction with metal surfaces, films of metallic phosphates, chlorides, and sulphides respectively, though with some types of phosphorus compound a phosphide film is produced. These films have shear strengths which increase in the order given so that the reduction of the coefficient of friction under boundary conditions below that found in unlubricated conditions decreases in the same order.

Since such materials operate only when a temperature has been developed on the surface which is sufficient partially to decompose the additive and release the active element, it is not really practicable to compare the coefficients of friction produced with such compositions with those resulting when compositions of quite different types are used. This is because the chemically-active additives take over when the films produced by other agencies are beginning to fail. The particular merit of the chemically-active materials is that films are produced which have a very high resistance to penetration by metal asperities, partly because of the mechanical properties of the surface film, and partly because of the high rate of chemical reaction which takes place at the appropriate time, thus rapidly repairing any breaches in the boundary film. Oils can be produced with chemically-active additives which allow adequate lubrication to be provided under those load and speed conditions which would lead to excessive friction, wear, and seizure with other lubricants.

Chemically-reactive additives, particularly those containing the elements chlorine and sulphur, must be selected to provide easy release of the active element when required without leading to corrosion in other regions of the lubricated component.

It has become the practice to refer to lubricants which provide surface films exhibiting the highest resistance to disruption (without necessarily providing low coefficients of friction) under boundary conditions as 'extreme pressure' oils, while those which provide low coefficients of friction are sometimes called 'boundary' lubricants. However, since both types provide lubrication under 'boundary' conditions this nomenclature is somewhat misleading. 'Oiliness' is another term which has come in for some abuse, but is now generally accepted as applying to that property of a fluid lubricant, usually associated with the presence of polar molecules, which enables it to reduce friction between and wear of surfaces in relative sliding motion under conditions in which no more than a negligibly thin film of lubricant can persist, namely in the regime of boundary lubrication.

In practice, the majority of lubricants designed to operate under boundary conditions will function by both adsorption and chemical reaction processes. Indeed, in the realm of extreme pressure lubricants it is common for a mixture of additives to be used to give optimum performance, small traces of some additives having a most marked synergistic effect on others. The mode of interaction with the surface, of a lubricant containing a number of additives, may involve a complex series of reactions; considerable light has been thrown on this subject by the use of radioactive tracer techniques. In its simplest terms the sequence of events when correctly chosen additive combinations are used appears to consist of adsorbed films giving way to chemically formed films in

the order—metal soaps, metal phosphides, metal chlorides, metal sulphides. In practice the transition is by no means so clear cut and the surface films will have very complex compositions at any instant.

Oils containing chemically-active additives have been most widely used for the lubrication of highly stressed gears, particularly those in which a high degree of sliding contact under high loads is involved. This condition applies, for example, in hypoid gears where two types of distress can arise. Failure of the lubricant film will lead to metal to metal contact and scuffing, while excessive surface stresses in the metals will produce metal flow and fatigue phenomena. Practical hypoid gear tests are designed so that hypoid oils can be formulated to minimize each type of distress. Present-day hypoid gear oil additive packages are largely of the sulphur/phosphorus type, the phosphorus additive providing effective lubrication, especially under low-speed, high-torque conditions.

In those gears where the slide/roll ratio is large without necessarily having the highest pressure conditions, oils producing low coefficients of friction are to be preferred. The use of castor oil based lubricants and more latterly polyglycols in worm gearing is a well-known example; in this instance the fatty or synthetic oil enables a higher efficiency to be achieved with a lower rate of wear and less tendency to the fatigue distress which arises when sliding occurs under conditions of high friction.

Solid lubricants such as graphite and molybdenum disulphide are effective boundary lubricants. These materials operate by interposing between the metal surfaces a film of laminae orientated parallel to the surface, the shear strength of the film in the direction of motion being very low. The adsorption forces in the case of molybdenum disulphide are said to be powerful and to operate through the sulphur atoms. Solid lubricants can be applied to the metal surfaces as dry films, sometimes with binding materials, which can then be lubricated with conventional oils. They may also be applied as dispersions in a lubricating oil carrier. In the first instance they suffer by being gradually worn away in service and in the second by having to be swept into the contact zone to be effective while at the same time being subject to sedimentation. Generally such solid materials find best application in high temperature or dry lubricant conditions, or when sliding speeds are extremely low but pressures are very high in, for example, fretting conditions where other types of lubricants are not particularly effective.

Solid lubricants of low shear strength are, as indicated above, often formed by the chemical interaction of additives with metal surfaces, while the oxide has a considerable effect on the sliding characteristics.

A wide variety of test machines have been proposed for the examination of lubricants under boundary conditions. Some find greater favour for testing certain lubricants because the test conditions bear resemblances to the conditions in the intended application, but some machines such as the four-ball machines are favoured, not so much for this reason, as for their simplicity and the reasonable repeatability and reproducibility of the results.

The method of reporting lubricant behaviour on most test machines is to state the load at which some particular effect occurs. In the four-ball machine, for example, the seizure and weld loads are used. The first represents the point when severe wear sets in, and the second when complete failure of lubrication occurs. The machine is also used for wear testing at a load below that at which

scuffing occurs, and wear scars developed on the balls are measured periodically.

Since the conditions imposed on the lubricant are different for every test machine and few exactly reproduce the conditions existing in practical applications, it has so far proved virtually impossible to obtain correlation between, or similarity in, the rating provided by the various test methods and in practice.

More recently a new class of additives known as friction modifiers have assumed some importance in attempts to achieve fuel economies from crankcase lubricants and emphasis has been given to formulating energy saving lubricants for certain industrial applications.

Expensive practical field trials are almost invariably essential to assess fully any new compositions or additives. However, engine and rig tests remain useful, after sufficient experience has been gained, for indicating approximately the sort of practical behaviour which might be expected.

CHEMICAL PROPERTIES OF LUBRICATING OILS

Oxidation

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant, this subject is probably the most thoroughly studied of any relating to lubricating oils.

Powerful agitation, which assists the diffusion of the gas throughout the liquid, heavy gas entrainment, particularly if the bubbles are of very small size so that the maximum liquid surface is presented to a given quantity of gas, and extended thin oil films or fine division of the oil phase as a mist so that the maximum liquid surface of a given volume of liquid is presented to the gas, are all factors which will increase oxidation rates. In common with most chemical reactions, the rate of oxidation is also profoundly influenced by the temperature; it is, in fact, approximately doubled for every 10–12°C rise in temperature above about 150°C.

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process.

Viewed chemically the reaction mechanism is known to be initiated by peroxide or hydroperoxide formation. The intermediate products are alcohols, ketones, and aldehydes. All the intermediate products on further oxidation lead to the development of carboxylic acids and hydroxy-carboxylic acids, while the aldehydic materials undergo complex condensation reactions. This generalization is of necessity a gross simplification of the many complex reactions involved, but organic acids and polymeric materials are the end products which particularly affect lubricant behaviour.

Pure paraffinic hydrocarbons tend to produce a higher fraction of organic acids than insoluble condensation products in the total amount of oxygen-containing materials produced. With aromatic hydrocarbons the reverse

applies. The development of oil-insoluble oxygen-containing condensation products, which are known as asphaltenes, is most undesirable in lubricating oils. Thus the popularity of high VI solvent refined oils of negligible aromaticity for engine lubricants and oils designed for use at high temperatures can easily be appreciated.

Another reaction mechanism which is particularly applicable to thermally initiated oxidation can be postulated as an energy chain mechanism. Energy-rich hydrocarbon molecules react with oxygen to produce energy-rich oxygenated products, which then transfer their surplus energy to further hydrocarbon molecules. This propagates the rapid growth in the number of activated hydrocarbon nuclei for oxygen attack. A free radical mechanism will also explain some other experimentally observed features of oxidation reactions.

The picture is further complicated by the effects of catalysts, which markedly increase the rate of oxidation. Autocatalysis is provided by peroxidic materials which are produced by thermal oxidation; once produced they markedly increase the oxidation rate by free radical formation. Metals such as lead, copper, and iron, amongst others, are notable for the catalytic influence they exert, an effect which is especially marked if these metals are introduced into the oil phase as metal soaps. These soaps can be progressively formed with the attack on metal surfaces by the organic acids formed in the early stages of oxidation.

With so many operative factors in the process of oxidation, it is not surprising to find that a vast range of materials has been proposed as oxidation inhibitors, functioning by various mechanisms. Some are 'chain-breakers' in that they prevent propagation of the chain of reactions by interfering with an intermediate step. Others have a particular ability to react rapidly with hydroperoxide in a manner that does not produce free radicals, thus removing a source of initiation of the chain reaction. Some compounds can carry out both functions. A less important type act as anti-oxidants by preventing or reducing the catalytic activity of metals by chelation, to form a non-reactive stable metal complex, or by forming stable films on metal and thus preventing its dissolution into the oil. In practice, most inhibitors are themselves oxidizable and tend to be consumed in the process of inhibition.

The inhibitors most used can be divided into two main classes: the first class includes oil-soluble materials containing sulphur or phosphorus, and the second consists of amine or phenolic compounds.

Sulphur compounds exist naturally in all lubricating oil fractions unless the latter have been so intensively refined as to eliminate all sulphur-containing materials. These naturally occurring compounds can act as oxidation inhibitors in their own right, and can also act synergistically with some of the aromatic compounds present, but their power in this direction is usually very much inferior to that of certain deliberately added sulphur-containing inhibitors such as sulphurized waxes or esters, aromatic sulphides, or alkyl phenol sulphides.

Phosphorus compounds such as alkyl and aryl phosphites, lecithin, and alkyl phosphates have also found application as oxidation inhibitors. Other compounds containing both combined sulphur and phosphorus are very popular oxidation inhibitors, typical examples being thio-ether phosphites and metal dithiophosphates. These are, as indeed are most inhibitors containing phos-

phorus and sulphur, dual-purpose additives in that they may also function as wear-reducing and load-carrying additives to degrees varying with the nature of the compound. Some inhibitors in this class which are the metal soap variety can also act as dispersancy additives.

Numerous inhibitors of this type, which are produced by the reaction of phosphorus pentasulphide with a variety of organic materials, have been proposed, but zinc dithiophosphates are now the most widely used anti-oxidants, especially in lubricants designed for use in internal combustion engines. In high temperature applications, zinc diaryl dithiophosphates may be preferred to the dialkyl types on account of their greater thermal stability, though they are not quite as effective in their inhibitive action. The effect on elastomers is also an important feature.

Oil-soluble organic amines and phenols such as phenyl-α-naphthylamine and 2,6-di-t-butyl-*p*-cresol are typical of the second class. Since these compounds are not effective at high temperatures, they are not normally used in engine lubricants, but they do find application in lubricants in which good oxidation resistance at moderate temperatures is required, for instance in steam turbine oils. However, certain hindered bisphenols, such as 4,4′-methylenebis-(2,6-di-t-butylphenol) are much more effective at high temperatures and are sometimes used in IC engine oils where an ashless oxidation inhibitor is preferred. In ester-based synthetic lubricants, particularly aircraft gas-turbine oils, both phenothiazine and some of its alkylated derivatives and derivatives of phenyl-α-naphthylamine have proved particularly effective, especially when used in conjunction with aromatic amines such as *pp*′-dioctyldiphenylamine.

A number of laboratory tests have been used for the assessment of oxidation resistance of lubricants. They usually consist of bubbling air or oxygen through the oil at a rate considerably higher than the rate of oxygen absorption by the oil and usually in the presence of various catalysts, of which metallic copper has been much the most popular, though increasing use is being made of soluble catalysts such as copper and iron naphthenates and mixtures of these. As purely relative rating tests they have proved extremely valuable, but since it is difficult on occasion to correlate the results with actual field performance it is common also to employ practical oxidation tests. In many internal combustion engine tests of crankcase oils the conditions are selected to produce oxidation of the oil; this may be achieved by artificially heating the crankcase oil in the sump to a temperature which will, in fact, be rarely if ever met in practice; the purpose is to assess the resistance of the lubricant composition to the development of oxidation sludge and lacquer deposits and the production of organic acids. The latter are capable of producing bearing corrosion problems.

In addition to those products formed during oxidation which have already been mentioned, carbon dioxide and water are associated final products of oxidative degradation. There is no fundamental difference between oxidation and combustion processes, except that the speed of combination of oxygen with the hydrocarbon molecules is higher in combustion and yields almost wholly the ultimate gaseous products carbon dioxide and water.

The speed of oxidation under initially moderate temperature conditions can be very high in oil mists and therefore the transition to combustion conditions with finely divided oil can take place over a narrow temperature range. The large surface area of the oil phase for oxygen uptake is one factor on which

comment has been made, but the heat developed readily produces vaporization and rapid temperature rise. Oil mists prove therefore almost as readily ignitable as hydrocarbon vapours and this is of particular relevance to the subject of crankcase explosions in internal combustion engines.

It has been shown that oil mists can be readily produced when crankcase oil comes in contact with a metallic surface at a moderately high temperature, for rapid volatilization and condensation to mist occurs; some thermal cracking of the hydrocarbon molecules also takes place to give volatile fragments. This mixture with air presents an explosion hazard as soon as the lower flammability limit is exceeded, and although ignition may not necessarily be initiated by the hot surface producing the mist it can result from a chance spark or blow-by. Support for the view that fuel dilution is not the only hazard is provided by the fact that crankcase explosions in gasoline engines are extremely rare.

A great deal of attention has been paid, particularly in marine circles, to the flash point behaviour of crankcase oils, because of its suspected relevance to crankcase explosions. It will be apparent, however, that moderate dilution of the crankcase oil by heavy diesel fuel is unlikely to be the major cause of crankcase explosions, although it must have some influence.

The ease of ignition of oil mists can also be responsible for the phenomenon of dieseling of air compressors, when crankcase oil escaping to the compression space past the pistons in the form of a mist is ignited on the compression stroke of the air compressor. This can motor the compressor, sometimes with disastrous consequences.

Corrosion

Lubricants must be formulated so as to avoid the promotion of corrosion by any of the ingredients or by their degradation products. They must also be able to prevent corrosion in certain sets of adverse circumstances when potentially corrosive contaminants come into the oil.

An example of the first condition arises with oil oxidation products, notably acids, which are capable of attacking many structural and bearing metals. Cadmium plated, and copper-lead bearings are notorious examples of potentially corrodible materials. The corrosive effect may be minimized in two ways; either the production of harmful peroxides and carboxylic acids can be inhibited, or the reactive metal surfaces can be isolated from the reactive materials with an appropriate film. In practice the oxidation inhibitors, such as zinc dithiophosphate commonly used in internal combustion engine oils, will function in both ways. The inhibitors will also be effective in preventing similar corrosion which might result with some combustion products finding their way past the piston into the crankcase.

Some sulphur compounds will prove very reactive towards certain metals, particularly cuprous and silver alloys, which can be applied as gearing or bearing metals. Objectionable black stains and even deep pitting can result from sulphur corrosion, while some tests indicate that fatigue life of the metals can also be adversely affected. A copper strip corrosion test is commonly applied to lubricating oils, but although mineral oils contain naturally occurring sulphur compounds capable of producing stains in this type of test, these are largely removed by modern refining processes such as solvent refining,

and base lubricating oils almost invariably give negative results. When additives incorporating active sulphur are used in gear and cutting oils, their general corrosive effect on non-ferrous metals can be minimized by metal deactivators which do not influence the performance of the additives under boundary conditions; mercaptobenzothiazole has been used for this purpose.

The most important aspect of contaminant-initiated corrosion is the effect of acids arising from the fuel used in internal combustion engines. The solution of sulphur acids from the combustion gases in condensed water is responsible for low-temperature corrosive wear in cylinders in diesel engines, and this has been greatly aggravated by the popularity of high sulphur content residual fuels in marine diesel practice. Protection from this type of corrosion is normally afforded by the incorporation in the lubricant of overbased detergent additives, often in proportions giving a relatively high degree of alkalinity to the oil, and reference has been made in an earlier section to highly basic type cylinder lubricants used with the same object.

A similar effect occurs in automotive gasoline engines, but in this case acids other than sulphur acids are, perhaps, even more significant. These are hydrochloric and hydrobromic acids arising from the lead scavengers in the fuel, and nitric acid resulting from the fixation of atmospheric nitrogen. Overbased detergent additives, used in smaller proportions, are helpful here, too, and ashless dispersants of the succinimide type also included in some motor oils have the ability to solubilize, rather than neutralize, acids and thereby assist in preventing their attack on metals.

In marine trunk piston engines, the contamination of the crankcase oil by sulphur acids has produced considerable corrosion problems, notably on the crankshaft journals and pins. This, however, has been largely prevented by the adoption of highly alkaline cylinder oils precluding the formation of acid scavenge drains.

Rusting of ferrous surfaces by water is another important contaminant-initiated corrosion effect. It can occur in marine diesel crankcases, where it may be aggravated by the saline nature of the water contaminant. Marine crankcase oils are, however, available with basicity to counteract acidity, as well as corrosion inhibitors of a type capable of being adsorbed on to the ferrous surfaces. Rusting is a problem, too, in steam turbines and in some hydraulic systems, and turbine and hydraulic oils normally contain corrosion inhibitors of which the most popular are long-chain dicarboxylic acids, such as alkyl succinic acid, and their salts or the products of neuralization of such acids by organic bases.

Such materials usually function by 'plating out' as adsorbed films on the ferrous surfaces, but have little influence in situations in which the surfaces are not normally wetted by the oil but can have water vapour condense on them. A number of corrosion inhibitors designed to function in the vapour phase have been introduced into steam turbine oils, and these include fairly long-chain carboxylic acids and amine compounds of such acids, but with somewhat mixed results.

ANALYSIS OF LUBRICATING OILS

Throughout this chapter reference has been made to additives and composition. Whilst quality assessment will be dealt with in a separate chapter it is

worth outlining some of the analytical techniques available to the lubricating oil formulator. Such techniques may be employed for quality control purposes; for the identification of additives; for the identification of base oils; and to assess the probable performance of a lubricant from its composition.

The usual physical and chemical characteristics of a lubricant will be evaluated by standard IP or ASTM test methods. Metal contents of additives such as calcium or zinc may be determined by chemical means although it is now more usual to employ atomic spectroscopic techniques such as atomic absorption or x-ray fluorescence spectrometry. The same analytical techniques will also measure chlorine, sulphur, or phosphorus in, for example, extreme pressure lubricants. Further identification and analysis of specific additives may be undertaken by infra-red spectrometry or one or more chromatographic methods. For example, thin layer chromatography and high-performance liquid chromatography are used successfully for identifying and determining alkyl phosphate, phenolic, or amine anti-oxidants.

Separation and concentration of high molecular weight additives such as the polymeric viscosity index improvers and pour point depressants, and the detergent or dispersant additives, may be achieved by dialysis through semi-permeable rubber membranes, whilst isolation of low molecular weight compounds, such as anti-oxidants and anti-wear additives, may be obtained by solvent extraction or adsorption chromatography. Further identification of the separated fractions is made by infra-red spectrometry, gas chromatography, or other chromatographic techniques.

Base fluids are normally characterized by a combination of analytical methods selected from infra-red, nuclear magnetic resonance or mass spectrometry, high performance liquid chromatography, and gas chromatography.

The analysis of a fully formulated lubricating oil must be conducted in a systematic manner. Much information may be gained from the physical tests and preliminary chemical information such as total base or acid numbers, saponification value and elemental analysis. Further detailed analysis is achieved by a careful selection of both separation and instrumental identification techniques pertinent to the lubricant being analysed.

CONCLUSION

The manufacture and the selection of lubricants for any application must be based on a consideration of the factors set out in the foregoing sections. There will be as many 'best' solutions as there are problems, and in fact, most lubricant suppliers market a wide variety of oils to meet requirements where one or other factor is especially emphasized. In practice, both in manufacture and in application, compromise is desirable in order to limit the number of lubricants. New materials are constantly being examined for their suitability as lubricants, and the search has been intensified in recent years by the demands of equipment especially in connection with the exploration of space where extremes of temperature and pressure are among the 'hostile environments' which are engaging so much attention. Reference has been made earlier to some exotic materials, the present high cost of which inhibits their use other than for very specialized applications, but which may find wider use as new and cheaper methods of manufacture encourage larger quantity production

bringing costs down further. However, oils of petroleum origin will, for many years to come, provide the basis for most of the fluids used in lubrication, with further developments in additives allowing them to cope with the more onerous conditions of operation imposed by modern engines and machinery.

An important influence on lubrication technique which has helped among other things in effecting a reduction in the severity of maintenance problems was the advent of what amounted to a new technology, namely Tribology, defined as 'the science and technology of interacting surfaces in relative motion and of related subjects and practices'. There is an awareness within industry of the importance of the interrelation of the many factors which Tribology covers, of the value of consultation between the experts in its various disciplines at the design stage in machine planning, and of the economies that such practices can achieve.

Many problems still face the lubricating oil technologist, and many more will undoubtedly arise as new engineering developments pose new lubrication problems and change the stresses on lubricant performance and properties and highlight quite new ones.

Some comment has been made on the need to use practical field trials of lubricating oil compositions designed for certain duties, and the effort involved in the testing of a modern lubricant is exemplified in the proliferation of engine test requirements which must be met by the modern crankcase oil. Table XVIII lists those current for the European and American vehicles.

TABLE XVIII
Engine Test Proliferation

European		American
Petter W-1	Fiat 600D	Caterpillar 1-H2, 1G2
Fiat 124AC	Ford Cortina	Caterpillar OL-1
DB OM 616	Peugeot 204	CRC L-38
MWM-B	Volvo B-20	Sequence IID
VW 1302	DB M102E	Sequence IIID
Petter AVB	Seal Tests	Sequence V-D

Each of the tests is designed to evaluate some particular facet of the oil's performance, for example sludge, varnish and rust formation, shear stability, bore wear, valve train wear, oxidation, etc. The development of more simple laboratory tests which would as reliably predict field performance remains an important area for further investigation, and the fact that past efforts in this direction have met with only very limited success should not discourage further attention to this matter. For example, several laboratories now use thermal analytical techniques, in particular Differential Scanning Calorimetry (DSC) to study the oxidative stability of lubricating oils and to provide rapid screening for expensive engine tests.

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27

Lubricating Greases

By F. E. H. SPICER

LUBRICATING grease is oil containing a thickener which modifies its flow properties. It is described by the American Society for Testing and Materials (ASTM) as 'A solid to semi-fluid product of dispersion of a thickening agent in a liquid lubricant'. The vast majority of greases are semi-solid materials made from mineral lubricating oils thickened with metallic soaps.

Greases may be used in preference to oil in applications where they can be expected to give satisfactory lubrication for long periods without the need for elaborate seals, pumps, or reservoirs. The flow pattern of grease within a bearing and the small quantity directly involved with lubrication result in little or no cooling effect. This is the main limitation to the use of grease as a bearing lubricant. By the proper selection of raw materials greases can be made which will satisfy applications ranging from bearings operating in the hard vacuum of outer space to the teeth of gears in a brick works. An acceptable grease life may be a few hours or several years.

GREASE COMPONENTS

Mineral oil is the cheapest and most commonly used liquid component of lubricating grease. Oil of almost any viscosity may be employed and the selection is governed by the intended use for the grease. Low viscosity base oils yield greases which will pump well, will give reduced bearing operating temperatures and may be used in low temperature applications. Heavier oils give greases which will lubricate better at lower speeds, will carry heavier loads and will assist when operating at elevated temperatures. The selection of oil viscosity for a grease-lubricated bearing is less critical than for an oil-lubricated bearing because there are no churning losses to be considered.

Synthetic oils may be used in greases where the need for special properties such as wide temperature range, oxidation stability, fire resistance, low volatility, or a high viscosity index outweighs the relatively high cost of these materials. Esters of dibasic acids, polyalkyline glycols, silicones, fluorosilicones, and similar materials are all used for this purpose.

Soap thickened greases contain a network of randomly oriented fibres up to 25 μm long as illustrated in Fig. 1. The fibres are formed by the controlled crystallization of soap prepared by reacting alkali or alkaline earth metal with a fatty acid. Oil is retained within this structure mainly by capillary forces in the interstices between the fibres. The alkali component may be calcium, sodium, lithium, barium, or aluminium, whilst the fatty acids are usually in the C_{10}–C_{30} range, and include mono-, di- and tri-unsaturated acids.

Some non-soap grease thickeners are particulate materials such as carbon blacks, organobentonites, silicas, terephthalamates, phthalocyanine, and other organic dyes. The particles of these materials have large surface-to-weight

FIG. 1. Electron micrograph of lithium soap (magnification × 20 000; reduced by 46 per cent in reproduction).

ratios and retain the oil by surface forces. Other non-soap thickeners are polymers such as polyethylene, polypropylene, and polyureas. These are believed to thicken by a fibre structure similar to soaps.

MANUFACTURE

Soap thickened greases are usually made by placing an alkali hydroxide with the fatty acid in a kettle containing a portion of the total oil required for the grease and a small amount of water. The materials are heated and react to form the soap. Excess water is then evaporated off and the temperature is raised so that the bulk of the soap goes into solution in the oil. This is followed by adding the remainder of the oil, and cooling with or without stirring, depending on the grease type. This is a very important stage during which the soap fibres are

formed. The grease is usually then homogenized or milled to improve the dispersion of the soap fibres in the oil. It is finally deaerated and packaged.

Manufacture of clay thickened grease is much simpler once the thickener is properly prepared. This preparation involves coating the clay particles, which are naturally hydrophilic, with a quaternary ammonium salt which makes them oleophilic. The coated clay is slurried in oil and an activator is added to cause the particles to disperse. Finally the product is milled and deaerated.

Dye thickened greases are produced by making a water dispersion which is mixed with the oil, dried and milled.

Polymer thickened greases are made by dissolving suitable blends of polymers in heated oil and cooling in such a way that a fibre structure is formed.

Manufacturing Equipment

Most greases are made by a batch production technique in kettles ranging in size from half a tonne to ten tonnes. Modern kettles are jacketed vessels with provision for heating and cooling the contents. They contain stirring and scraping paddles, and are often fitted with an external pumping system to give bottom to top circulation, thus ensuring good mixing and heat transfer from the kettle walls to the contents. The whole manufacturing process can be performed in an open kettle at atmospheric pressure, but it is more common to use closed kettles (autoclaves), operating at up to 10 bars, for the saponification stage, then to transfer the product to open kettles for cooling. This is a much quicker method of manufacture and one autoclave can frequently be used in conjunction with several open kettles. A grease plant of this type is shown in Fig. 2.

Recently, continuous production techniques have been developed for soap thickened grease manufacture. In one process, all the heat required is supplied to the oil alone. The saponification takes place in a reaction vessel subject to high shear mixing, and the product from this stage is passed through an expansion chamber to flash off the water. Subsequent cooling is achieved by adding cold oil to the dehydrated soap concentrate in a low shear mixer. The final product tends to contain very little air compared with conventionally made grease. This manufacturing process is illustrated in Fig. 3. It is attractive because the system holds only a small quantity of grease, and switching from one type to another entails much smaller cleaning losses than in batch production.

Mills and homogenizers improve the distribution of the thickener in the oil, and help to produce a smooth and uniform material. In principle they function by forcing the grease through a narrow aperture at a high shear rate. High-speed mills have a gap of up to 600 μm between a stator and a rotor which rotates at 2000 to 3000 rev/min. Homogenizers are reciprocating pumps which are used to force the grease through narrow orifices at pressures up to 200 bars.

Raw Materials

The raw materials used to make grease govern the properties of the product and hence its end use. Properties such as shear stability, water resistance, temperature stability, and tackiness are affected by the metallic radical of the soap. Only the most important of these will be described.

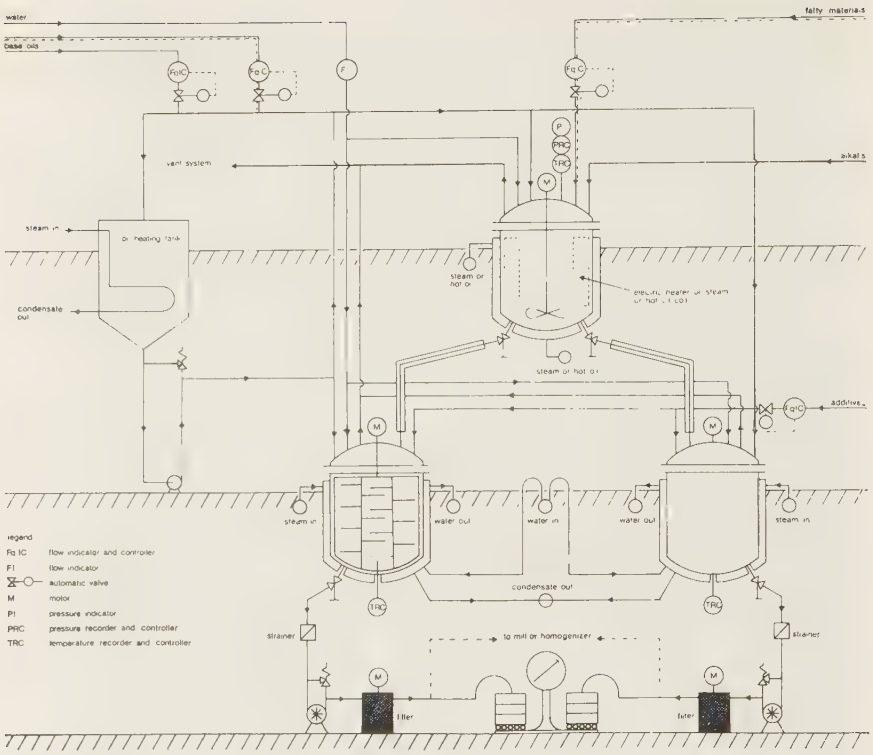

FIG 2. Typical layout of grease plant.

Calcium Soap Greases

Conventional calcium base greases are made by reacting hydrated lime with fatty acids prepared mainly from animal fats. Water is an essential component of the salt crystals forming the fibre structure of this type of grease. The quantity of water required depends on the raw materials used, but may be up to 1 per cent. Once the quantity drops below 0.2 per cent the crystal structure breaks down. This limits the use of conventional calcium base grease to applications where the temperature does not exceed 60 to 70°C. Above this temperature grease life is unacceptably short. The performance of calcium base greases is not greatly affected by the presence of up to 50 per cent of water dispersed in the grease. They are relatively cheap and effective lubricants within the temperature limitations defined, and constitute about one-tenth of the total grease volume sold. This market share has dropped considerably over the past thirty years as demand for products with higher temperature limits has increased. This trend will undoubtedly continue as the rising cost of mineral oil represents a larger proportion of the cost of the grease, and the contribution of the cost of the soap therefore declines.

Anhydrous calcium soap greases can be made in which the soap may be formed from more expensive fatty acid components, e.g. 12-hydroxystearic acid. Such greases are not subject to the temperature limits of water-stabilized greases.

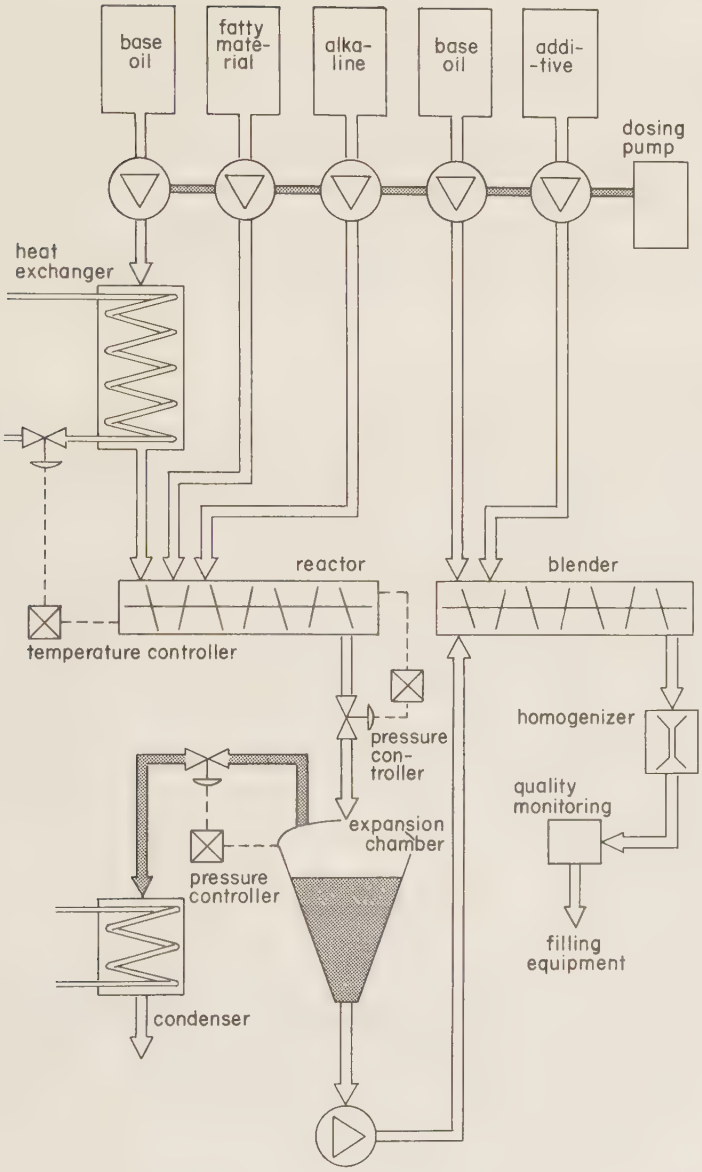

FIG. 3. Continuous unit flow diagram.

Sodium Soap Greases

Historically, sodium base greases were developed in order to provide a material which would operate at higher temperatures than calcium base greases.

They are made by saponifying sodium hydroxide, caustic soda, with fats of which tallow is the most common. There is no significant water of crystallization in the soap, so the temperature limitation associated with this does not apply to soda base greases. However, at temperatures in the range 90°C to 120°C irreversible changes occur in the soap structure and the grease hardens, making it unsuitable for use at these temperatures. A further restriction on the use of soda base grease is brought about by the solubility of the soap in water. Small quantities of water can be absorbed by the grease, which are claimed to offer some protection against corrosion, but large quantities will dissolve the soap and break down the structure of the grease.

Lithium Soap Greases

Over half of the total quantity of grease manufactured in the free World is based on lithium soap. It is important to differentiate between lithium 12-hydroxystearate thickened greases, which are strongly resistant to shearing, and lithium stearate greases which are not. Lithium hydroxystearate greases are widely used in ball and roller bearings where lithium stearate greases would probably break down and leak out.

Lithium hydroxystearate grease is usually manufactured by reacting lithium hydroxide with hydrogenated castor oil or 12-hydroxystearic acid. Satisfactory greases can be made from a wide variety of base oils. By selecting suitable mineral oils greases can be made which will give good lubrication at −50°C or at +140°C. Synthetic oils may be thickened with lithium hydroxystearate to make greases for operation at temperatures between −55°C and +200°C.

In addition to their good shear stability and potentially wide temperature range lithium base greases are very water resistant. In other words water will not affect the structure of the grease. They are therefore eminently suitable as multi-purpose greases in a wide range of applications.

Complex Greases

Most commercial complex greases are thickened with particles or fibres formed by reacting two dissimilar acids with a single alkali. Thus a calcium complex grease can be made from lime, a fatty acid, and acetic acid. Similarly, complex greases may be made with sodium, aluminium, and lithium. These greases melt at a considerably higher temperature than the simple metal, fatty acid soap materials, and are becoming increasingly popular for applications such as steel mills and automotive wheel hub bearings.

Clay Thickened Greases

The particles of naturally occurring clays such as bentonite and hectorite may be suitably coated and used as thickeners for greases which do not melt. Unfortunately the coatings are sensitive to some additives and, over extended

periods, to some oxidation products; hence clay thickened greases may be made for operation at very high temperatures but only for relatively short durations.

Polymer Thickened Greases

Both polyethylene and polypropylene may be used to produce greases from suitable base oils. Each polymer imparts different properties to the grease. By judicious balancing of these materials semi-fluid greases may be produced with a robust structure, low thickener content, and good oil retention. Since the polymers will dissolve completely in mineral oil at about 140°C the operating temperature for such greases will not exceed 100°C.

Polyurea greases made by reacting amines with isocyanates have good high-temperature properties and may be used in similar applications to those satisfied by complex and clay thickened greases.

ADDITIVES

The natural properties of greases may be enhanced by the introduction of additives which need not be oil-soluble at the working temperature of the grease.

Most greases have some inherent rust-inhibiting properties, but these can be improved by the addition of oil-soluble materials such as metal naphthenates or finely divided solids such as sodium nitrite.

The service life of greases at elevated temperature is often limited by the oxidation stability of the base oil. This can be extended by the use of suitable amines, substituted phenol, or zinc dialkyl dithiophosphate. Certain metals used in bearing manufacture are known to catalyse oxidation, and it is sometimes necessary to add a metal passivator such as benzotriazole to grease to improve oxidation resistance. Calcium complex greases have inherent extreme pressure, EP, properties, i.e. they are capable of preventing gross dámage to rubbing surfaces even though the grease film is substantially broken. Nevertheless, lead, sulphur, chlorine, or phosphorous additives may be added to these greases, as they are to other soap thickened greases and to polymer thickened greases to enhance their load carrying ability. In applications where speeds are very low and loads are high solid lubricants such as molybdenum disulphide, and graphite are effective additives.

It is occasionally necessary to improve the cohesive and adhesive properties of grease when, for example, it is required to adhere to small gears or to be used as a chassis lubricant on some vehicles. This can be achieved by the addition of a material such as polyisobutylene.

GREASE PROPERTIES AND TESTING

The performance of grease is governed by properties which can be controlled during manufacture but cannot usually be assessed until the grease is substantially finished. For example the hardness, consistency, of a grease is dependent upon the thickener content, but is also affected by the heating cycle

used in the manufacturing process and the degree of homogeneity achieved in the final milling stage. Consistency can be measured fairly quickly and greases can be softened by the addition of oil to the finishing kettle. Properties such as oxidation stability, shear stability and lubrication, however, can only be assessed after tests lasting many hours. Thus development of grease formulations and manufacturing techniques is a time-consuming process.

Consistency

Consistency is a measure of the hardness of a grease and, as indicated earlier, depends mainly on the proportion of thickener in the base oil. It is an important factor in assessing its suitability for a given application. Hard greases cannot easily be pumped and are therefore unsuitable for use in bearings requiring frequent re-lubrication. Soft greases can be pumped over considerable distances, but are unsuitable for large bearings or in bearings subject to vibration.

Consistency measurement has been standardized by the ASTM and the IP in their joint method ASTM D217/IP50, or D1403/IP310 for small samples. It is achieved by measuring the depth to which a free-falling standardized cone will penetrate a grease sample at 25°C in five seconds. This measurement, in tenths of a millimetre, has been graded by the National Lubricating Grease Institute of America, the NLGI, as shown in Table I, and it is usual to classify a grease by its NLGI grade. Each grade covers a range of 30 points, and there is a 15-point separation between the grades.

Greases in the 000 and 00 grades are semi-fluid greases which, in bulk, will flow under their own weight. They are mainly used as gear lubricants in applications where the use of oil would give undesirable leakage and where heat transfer requirements are not particularly severe. Grades 0, 1, and 2 greases may be used in bearings requiring frequent re-lubrication through a centralized grease lubrication system. Greases in grades 2 and 3 are the most commonly used materials for ball and roller bearing lubrication. Bearing size is usually the governing factor in deciding which grade to select. In general terms it can be said that grade 2 greases give slightly better lubrication in smaller bearings and grade 3 greases will be more suitable for bearings with a bore diameter greater than about 100 mm. Grades 4 and 5 greases are not freely

TABLE I
NLGI Grease Classification

NLGI No.	Worked penetration
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

available and are used where their sealing properties are as important as their ability to lubricate. Grade 6 greases are normally made in rectangular blocks and are used by being spring-loaded against plain bearing journals.

Shear Stability

It is usually important that greases should not suffer significant changes in consistency, either hardening or softening, as an effect of shearing. An initial assessment of this can be made by measuring the change in consistency which occurs when a perforated plate is forced up and down through a sample in a grease worker for a specified number of strokes. This is referred to as the worked or prolonged worked penetration in ASTM D217/IP50. Another test for the same property is the Roll Stability test ASTM D1831. Neither of these tests provides a reliable prediction of the stability of a grease under the very severe conditions which can obtain in some rolling bearings.

Drop Point

The drop point can be used to assess whether a grease of known formulation has been properly made or to obtain an indication of the type of thickener which has been used in a grease of an unknown formulation. It cannot be used to measure the upper operating temperature limit for a grease.

The standard drop point tests ASTM D566/IP132 and ASTM D2265 indicate the temperature at which the thickener is so soluble in the base oil that the grease becomes substantially fluid. Clay and dye thickened greases have no measurable drop points.

Oil Separation

Some separation of oil from a grease is unavoidable and is believed to be necessary for its success as a lubricant. Excessive separation indicates a badly made grease.

Two tests for oil separation are commonly used, ASTM D1742 and IP121. These tests are similar in principle but different in detail, and would not be expected to yield the same value for a given grease sample. Both measure the separation of oil from a grease under a small pressure gradient.

Oxidation

Inadequate oxidation stability of a grease may lead to hardening, softening, oil separation, or the generation of gum and lacquer deposits. No standardized tests are available which will accurately predict the resistance of grease to oxidation in service or in storage. The oxygen bomb test IP142/ASTM D942, which measures the absorption of oxygen by a grease sample in a pressurized container, can be used to monitor the quality of a grease formulation of known performance or storage characteristics.

Water Resistance

It is often essential for grease to be able to lubricate in the presence of water. Some greases, particularly calcium-based materials are capable of absorbing a fairly large proportion of water without a significant reduction in performance. Others like lithium greases absorb very little water and are not affected by its presence.

A test for the ability of grease to remain in a bearing in the presence of water is the IP215/ASTM D1264 water washout test. This is performed by projecting a jet of water at 38°C or 79°C, against the unsealed housing of a rotating bearing and measuring the grease weight loss. The test measures only the resistance of the grease to being washed out and does not reflect the lubricating properties of the grease in the presence of water.

EP (Extreme Pressure) Properties

Under suitable operating conditions grease will produce a hydrodynamic lubricant film, but where load and speed conditions do not allow this provision must be made to reduce damage to rubbing surfaces by the introduction of EP additives into the grease. These tend to be necessary in low-speed/high-load applications and under shock loads. Gears in particular often require lubricants containing EP additives.

An indication of the effectiveness of EP additives in grease can be obtained by testing on the Timken Wear and Lubricant Tester by the IP326/ASTM D2509 method. In this method a rectangular steel block is loaded against a rotating steel ring lubricated by the test grease. The load is increased by stages until gross damage occurs to the test pieces. The maximum load which can be applied without producing this damage can therefore be determined. It is referred to as the OK load. The IP239 and the ASTM D2596 four-ball EP tests have similar test-piece configurations, namely three fixed balls loaded against one rotating ball. Operating speeds and load stages are different, however, and the resulting wear and load carrying parameters give slightly different figures. Four-ball EP tests will not always rate greases in the same order as Timken EP tests, and it is necessary to determine which test correlates better with the given application before deciding to use one in a specification.

Rheological Properties

Greases are non-Newtonian materials. At high shear rates the viscosity of a grease approaches that of its base oil, while at shear stress levels below the yield value grease will not flow at all. These are useful properties, since in the high shear rate region within bearings and gears grease behaves in a similar way to oil, whereas in the covers and housings, where the shear stress is low, grease tends to act as a seal.

It is difficult to measure the rheological properties of grease over the wide range of shear rates and shear stresses encountered in service. Nevertheless, it is necessary to obtain flow curves over the appropriate temperature range for any grease which is to be pumped through a lubrication system. Without these it is

not possible to calculate pipe dimensions and system pressures. The ASTM D1092 method involves the use of an apparatus in which flow rates through steel capillaries are related to pump pressures. It is mainly used at low temperatures and has weaknesses at shear rates below 10 sec^{-1}. In recent years, cone and plate viscometers have been employed to obtain similar data which have been used in conjunction with a series of charts published by the NLGI as an aid to calculations associated with pumped grease systems.

Bearing Performance Tests

The only satisfactory method of predicting grease performance in rolling bearings is to undertake simulated service trials under controlled conditions in a laboratory. Three standardized methods are commonly used for this purpose. The ASTM have developed method D1741 in which 30-mm ball-bearings are used and D3336 in which 20-mm ball-bearings are run at elevated temperatures until excessive torque indicates inadequate lubrication.

In the IP168 method wear of the bearing elements, grease weight loss, and changes in consistency after a 500-hour test, in a 40-mm bearing, are used to assess the quality of greases. The test may be run with the bearing at its natural operating temperature or with its temperature raised by additional heating and at speeds in the range 1000 to 10 000 rev/min.

Many bearing manufacturers test greases under a variety of loads, speeds, and temperatures in apparatus of their own design.

Compatibility

It is never advisable to mix greases of different thickener types or greases made by different manufacturers. Mixing sodium base greases with greases made from other thickener systems will usually result in the loss of structure of the mixture. Similarly, mixing clay thickened greases with greases containing certain common additives will impair the efficiency of the thickeners. These phenomena depend not only on the types of greases that are mixed but also on the proportions of the mixture. Testing is protracted since several different mixture ratios must be examined at various operating temperatures.

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28

Petroleum Waxes

By F. JOWETT

INTRODUCTION

Waxes from mineral sources have been known for well over a century. The discovery of wax in wood tars took place about 1830, and by 1833 a wax was being separated from crude oil seepages in Burma.

The first production of wax was by the destructive distillation of Scottish shale oils, and such wax was certainly being used in the preparation of candles as long ago as 1850.

The first recorded commercial petroleum wax production from crude oil appears to have been in Pennsylvania, USA in 1867, less than ten years after the first oil well was drilled at Titusville in the same State. The separation of wax from the crude oil was effected by hanging canvas bags of chilled oil in a commercial refrigerator, the solid wax remaining behind in the bag filter whilst the oil dripped out.

A mineral earth wax, called ozokerite, was discovered and mined in Galicia, with the largest mines being in the northern foothills of the Carpathians. Refining of this product by sulphuric acid, followed by treatment with animal charcoal produced a pale yellow product given the name ceresin, a name still sometimes applied to mixed petroleum waxes, although the genuine ozokerites and ceresines have virtually disappeared.

The present petroleum wax industry resulted from demands for lubricants with better low-temperature properties, since at these low temperatures any wax present in the oils then in use would separate, and thus reduce the fluidity and effectiveness of the lubricant. Originally, therefore, petroleum wax was an unavoidable and unwelcome by-product arising from the dewaxing of lubricating and gas oils, but as more and more applications for this product were found, wax became to be a primary product in the refining operation.

MANUFACTURE AND CLASSIFICATION OF PETROLEUM WAXES

A schematic representation of the basic routes by which petroleum waxes are produced from crude oil is given in Fig. 1.

These different routes by which separation is accomplished have given rise to three wax classifications namely, paraffin waxes, intermediate, and microcrystalline waxes.

Paraffin and intermediates are sometimes referred to collectively as 'distillate' waxes. Whilst serious and lengthy attempts have been made to define physical and chemical boundaries between these groups, none has succeeded.

Paraffin waxes are mixtures of saturated paraffinic hydrocarbons (alkanes), straight-chain or 'normal' alkanes being by far the major components of the mixtures, with varying proportions of paraffins having a degree of branching in

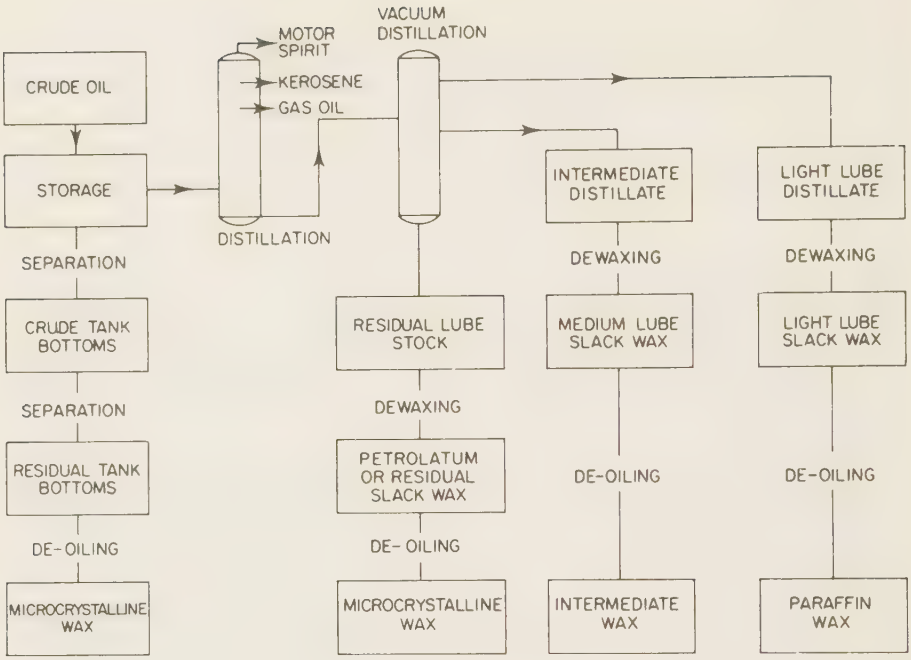

FIG. 1.

their chains (iso-alkanes) present, together with a small cycloalkane content.

The chain length of the individual alkanes ranges from about 18 carbon atoms to about 45, the higher the average molecular weight of the alkane mixtures, the higher the proportion of iso-alkane likely to be present.

Such regular arrays of straight-chain molecules lend themselves to symmetrical packing or crystallization, this being the outstanding characteristic feature of these waxes.

Intermediate waxes are essentially very similar, with individual alkane chain lengths of up to 60 carbon atoms, with higher average molecular weights, and with branched-chain components up to about 50 per cent of the whole.

Microcrystalline waxes also are mixtures of saturated alkanes, but with a much greater preponderance of branched-chain or cyclo molecules. The carbon atom content per molecule can vary from the mid-thirties to well over eighty, the average molecular weight thus being much higher than in the case of the distillate waxes. The complex branched-chain structure prevents any degree of close packing and macrocrystallization, giving rise to the original name of 'amorphous' waxes, and later, rather more accurately, to the current nomenclature of 'microcrystalline' waxes.

Thus from the narrowest cut and the lowest average molecular weight paraffin wax, to the widest molecular weight spread of complex hydrocarbons comprising a microcrystalline wax, there is a continuous spectrum of commercial waxes with no clear demarcation lines capable of being drawn between these classifications.[1]

PRODUCTION OF PETROLEUM WAXES

Distillate or Paraffin Waxes

Since the bulk of paraffin wax present in crude oil boils over the same range as lube oil distillates, separation by distillation is not possible. Consequently the bulk of lube oil dewaxing is carried out by means of crystallization from a suitable solvent system. Mixtures of toluene and methyl ethyl ketone are generally used, although other mixtures and some single solvent systems such as methyl iso-butyl ketone, methyl n-butyl ketone, and propane are sometimes used.

The waxy oil feed is mixed with the appropriate solvent system and heated to a temperature sufficient to bring about complete solution of the wax. Cooling this solution causes the wax to separate, and when the mixture has reached the chosen low temperature it is passed to rotary vacuum filters where the solid is separated from the liquid in the form of a thin cake. This is washed with chilled solvent and then removed from the drum by being blown off the filter screen by inert gas. The solvent-containing filter cake is then either retreated with further mixed solvent in the process of 'de-oiling' (see later), or transferred to the 'slack wax' storage by way of steam strippers, which effect solvent stripping and recovery. The solvent-free slack wax is then stored for sale or further processing.

The slack wax thus produced is generally brown in colour and has an oil content of between 5 and 25 per cent.

Alternative solvent systems employing high specific gravity chlorinated hydrocarbon solvents (the 'SN' process and the 'Bari-Sol' process), which allow separation of the slurry to be carried out by centrifuging rather than by vacuum filtration have been used in the past, but these have been largely superseded by the MEK-toluene process.

A more recent technique[2] using mixed ketone solvents, but achieving chilling by incremental dilution with cold solvent, claims much improved efficiency, with subsequent ease and lower cost of further de-oiling. This process, called the Dilchill dewaxing process,[3] was adopted at several refineries in the USA in the 1970s.

The dewaxing operation removed a relatively small proportion of wax components from a large proportion of oil to produce slack wax. The next stage, de-oiling, removes oil from a larger amount of wax, to give waxes of low oil content and commercially acceptable specification. Two methods are currently in use:

(a) Solvent de-oiling. This is much the most widely used method, the normal solvent system again being methyl ethyl ketone-toluene.

As in dewaxing, the feed is diluted with solvent in a suitable ratio and dissolved by heating. On being cooled, as before, to a predetermined temperature, the wax separates and is filtered. Cooling further to lower temperatures gives further wax separation, the average molecular weight and melting point of this and any subsequent fractions being lower.

Each wax cake thus produced is remixed with further cold solvent, filtered and solvent washed, the solvent at all times being separated and re-cycled.

The ultimate oil content of a fully refined paraffin wax should be less than 0.5 per cent (see Methods of Testing Petroleum Waxes below).

(b) De-oiling by sweating. The feedstock chosen as suitable for the sweating process is first melted to produce a homogeneous liquid, then cooled under conditions calculated to give a wax cake of coarse crystal structure. The temperature of the cake is raised slowly in a controlled manner in equipment designed to allow liquid components to drain away while retaining the higher melting solid residue of the cake.

The process thus removes not only the liquid oil, but also reduces the content of the iso-paraffins, which are of lower melting point than the normal alkanes of corresponding molecular weight, and it thus achieves a measure of fractionation at the same time as de-oiling.

The structure of the wax cake in the sweating process must be coarsely crystalline, otherwise the oil is retained by capillary forces. Slack waxes containing too high an iso-alkane content give a relatively fine crystalline structure, and thus cannot be de-oiled by this method.

Sweating has largely been replaced by the solvent process, but more recent developments[4] suggest that the operation will continue in small units of high efficiency and low running cost.

Intermediate and Microcrystalline Waxes

Separation of these waxes from the intermediate lube distillate, the residual lube stock, and the tank bottoms, follows an essentially similar series of solvent extraction steps as for the distillate waxes. It is not possible to refine either type by traditional sweating techniques, nor can the measured oil contents of the microcrystalline range be reduced to such low levels as is standard with the paraffin waxes.

The final stage of refining all types of petroleum waxes to remove odour, taste, and colour, and thus to purify the wax to a standard complying with the various regulations covering usage in, or in contact with foodstuffs, is referred to as 'finishing'.

A variety of processes is in current use, percolation through activated clay or bauxite still being used for all types of petroleum wax.

A more modern and versatile finishing treatment is the technique of hydrogenation, known as hydrofinishing, where wax, in its final form or as slack wax, is treated with hydrogen in the presence of a catalyst at high temperature and pressure. Various hydrofinishing processes employ different catalysts operating under different conditions, with pressures ranging from 10 through a typical 85 to 200 atmospheres, and temperatures from 200 to 400°C. The process is one of chemical saturation, with virtually complete sulphur removal, optimum conditions producing a white odourless wax meeting highest purity standards, and requiring no further finishing treatments.

Paraffin waxes may also be treated by the so-called 'acid-earth' process where agitation of the molten wax with a few per cent of sulphuric acid is followed by separation of an acid sludge, and a treatment with neutralizing lime and activated earth. This process is not possible for microcrystalline waxes, because of the difficulties in separation of the acid sludges produced, and is now not widely used, almost all refineries having adopted hydrofinishing processes.

COMPOSITIONS OF PETROLEUM WAXES

Paraffin and Intermediate Waxes

The chemical composition of petroleum waxes, to which reference has already been made, has become very much clearer in recent years.

The first attempts to elucidate the constitution of the simpler distillate waxes were by combinations of distillation and repeated fractional crystallizations to effect separations of individual or groups of components, and give a superficial picture of their constitution.

A step further in distillate wax analysis came with the discovery by Bengen that urea is capable of giving crystalline adducts with normal alkanes,[5] where the urea molecules form a hexagonal prism enclosing an internal channel in which the linear portion of the hydrocarbon can fit.[6] However, iso-alkanes with short side chains will also be adducted, provided that the branches are near the ends of the chains.[7]

The development of high-temperature mass spectrometry, notably by O'Neal and associates,[8] was a major step forward in unravelling the detailed structure of paraffin waxes, but undoubtedly the technique which has done most to elucidate the composition of the light and intermediate distillate waxes has been high-temperature gas–liquid chromatography (glc).

The use of liquid phases capable of operating to 400°C and above allows normal alkanes of up to 60 carbon atoms to be detected and quantified. By the use of pure internal standards in combination with a standard analytical run, the normals content of a distillate wax may be estimated, and information obtained on the non-normals distribution. The chromatographic analysis of paraffin waxes is now established as a routine operation of good precision.[9]

Figures 2 to 4 are the glc traces obtained on three typical distillate waxes, showing the carbon distribution of the alkane components of the waxes. The small peaks immediately before the main normal alkane peaks are those of the 2-methyl alkanes, whilst the unresolved area below the trace is proportional to the amount of more heavily branched non-normal hydrocarbons present in the wax.

The actual branched or 'non-normal' content of petroleum waxes can be determined quantitatively by adsorption of the normal alkanes using type 5A Linde molecular sieve.[10]

This synthetic zeolite is a crystalline calcium alumino silicate having a crystal pore diameter of 5 ångströms into which straight-chain hydrocarbon molecules with a critical diameter of less than 5 Å are adsorbed. Branched-chain hydrocarbons are not adsorbed. Thus there is provided the basis for a highly selective and quantitative separation technique. When used in conjunction with glc to monitor the progress of the several extractions which may be necessary in the case of the higher non-normal content intermediates, the sieve analysis–glc technique provides detailed quantitative information on wax composition.

The figures recorded for non-normal contents of a wax are always higher than for those recorded on the same wax by urea adduction, for reasons stated earlier.

The thermoanalytical technique of Differential Scanning Calorimetry (DSC) is a further aid to the investigation of petroleum wax properties and

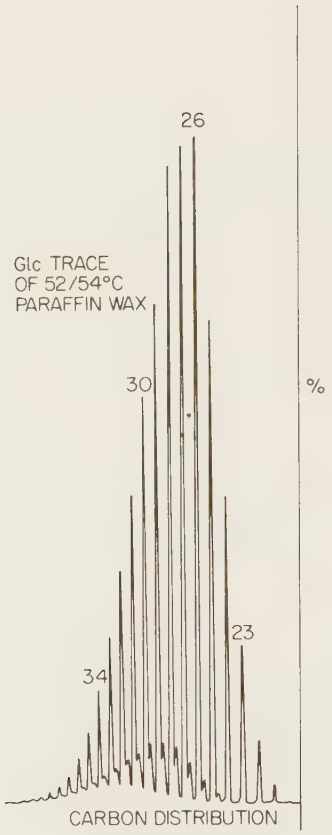

Fig. 2.

composition, providing a highly characteristic record of the melting and crystallization behaviour of a wax, measuring directly energies associated with solid–solid and solid liquid transitions.

By associating the individual heats of fusion for the specific hydrocarbons detected and quantified in a wax by glc analysis, Faust[11] has been able to calculate its degree of crystallinity, a factor which has considerable bearing on the rheological and bulk properties of that wax.

Residual or Microcrystalline Waxes

Knowledge of the composition of microcrystalline waxes is much less advanced than for distillate waxes, because the high molecular weight of this type of wax makes it less susceptible to analysis. In particular, whilst the vast number of isomers of any given carbon number renders resolution by glc impossible, and the determination of the small normals content difficult, the excessive temperatures and times needed to clear the columns of retained hydrocarbon makes the attempt highly undesirable.

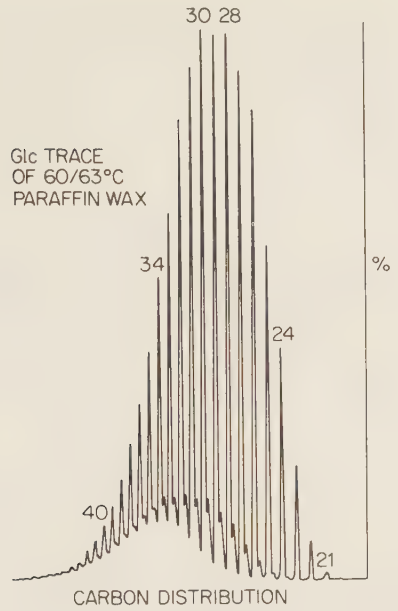
30 28
Glc TRACE
OF 60/63°C
PARAFFIN WAX
34
%
24
40
21
CARBON DISTRIBUTION

FIG. 3.

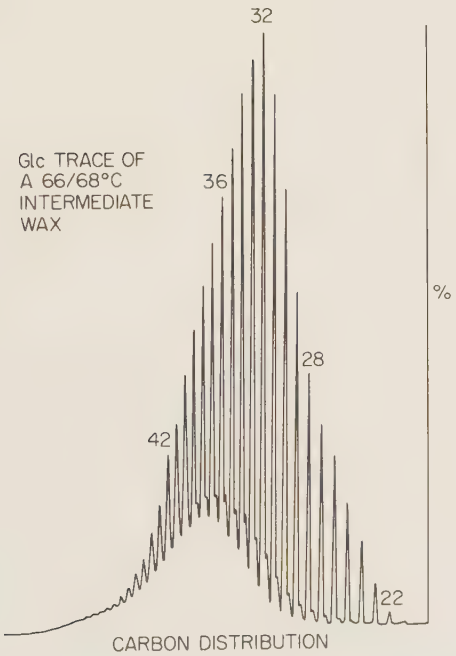
32
Glc TRACE OF
A 66/68°C
INTERMEDIATE
WAX
36
%
28
42
22
CARBON DISTRIBUTION

FIG. 4.

Some of the most detailed analytical work has been carried out on Middle East and Venezuelan crudes,[12] and confirms that the microcrystalline waxes from these materials are composed mainly of multiple-branched iso-paraffins and monocycloparaffins. The analytical separations in this work were based on pyrolysis, hydrogenations, and gas-liquid chromatography.

Petrolatum

The mixture of microcrystalline waxes and high molecular weight oil produced by dewaxing a de-asphalted vacuum distillation residue from a crude oil is usually termed a 'residual slack wax', but equally, it may be thought of as a crude petrolatum.

Refining, without further de-oiling, by using the same techniques as for microcrystalline waxes can produce a Pharmacopoeia grade petrolatum or petroleum jelly.

PHYSICAL PROPERTIES OF PETROLEUM WAXES

Distillate Waxes

Since straight-chain alkanes are the major components of these waxes, it is natural that the many detailed studies on pure normal alkanes which have been made should be used as reference criteria in the investigations into the physical properties of the waxes themselves.

The straight-chain alkanes in the range from 20 to 36 carbon atoms are known to show transition points in the solid phase.[13] This means that at least two modifications are known, stable at different temperatures and with different crystal habits, and numerous workers have investigated these crystalline forms of the pure or purified alkanes.[14,15,16]

Mazee[17] investigated binary mixtures of alkanes of adjoining or near adjoining carbon numbers, and found a continuous series of mixed crystals, the equilibria between the two solid phases showing pronounced maxima in the transition range. However, if the alkanes differ by many units in chain length no mixed crystals are formed, but a normal eutectic is observed, and, as expected, in paraffin waxes the same phenomenon is recorded.

Barmby *et al.*[18] were able to study these transitions in paraffin waxes by a combination of X-ray diffraction, differential thermal analysis, and dilatometric techniques, and demonstrated that two solid–solid phase transitions would occur in low melting point wax, a single transition in higher melting point waxes, and no such transition in paraffin waxes of highest melting point.

This endothermic transition from the onset of the solid–solid transition to the completion of melting can be followed easily and in a quantifiable manner by differential scanning calorimetry, and rather more laboriously by plotting the cooling curve, illustrated schematically in Fig. 5.[19]

The wax is liquid at A, and as the temperature falls through the plateau melting point B–C (the first-order transition point), the material changes from liquid to a solid having a hexagonal crystalline structure. As the temperature continues to fall the crystalline structure changes exothermally from hexagonal to orthorhombic at D, the second-order transition point.

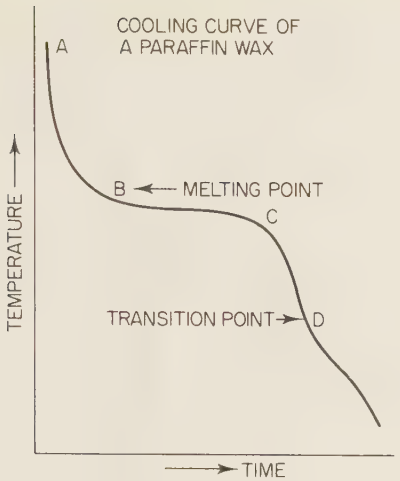

Fig. 5.

The DSC scan of the same type of paraffin wax produces a more easily recognized second order transition, together with a sharp melting peak.

These phenomena are readily observed with the lower melting point waxes previously referred to,[18] i.e. where the mass of the carbon chains are of low carbon number, but as the average chain length increases, the temperature range in which the hexagonal lattice is stable becomes narrower, the second order transition moving nearer and nearer to the melting point.

With a substantial proportion of 30 and more carbon atoms per molecule present in the wax the hexagonal lattice is not clearly defined, and with increasing average chain length there is a direct crystallization from the liquid into the orthorhombic structure, and the transition is not seen.[20] This can be seen in Figs 6 and 7.

Figure 6 shows the DSC scans recorded on four low melting point paraffin waxes produced from the same light lube slack wax, the same weight of wax being used in each case, the scan zero being displaced vertically for ease of comparison. It will be noted that the lowest melting point wax shows two solid–solid transitions.

Figure 7 demonstrates the disappearance of the solid–solid transition with increasing average chain length and melting point. Again waxes from the same refinery are used to show that a 54/57 °C wax has the characteristic solid–solid transition, whilst in a 60/62 °C wax this has almost been absorbed in the melting peak. The 63/66 °C wax shows no transition, and on cooling, crystallization into the orthorhombic state would occur.

Microcrystalline Waxes

Since above about C36 even normal alkanes crystallize directly from the melt into the orthorhombic state, it is to be expected that microcrystalline waxes, containing much higher molecular weight hydrocarbons with high non-normal contents, will fail to show second-order transition points. Furthermore,

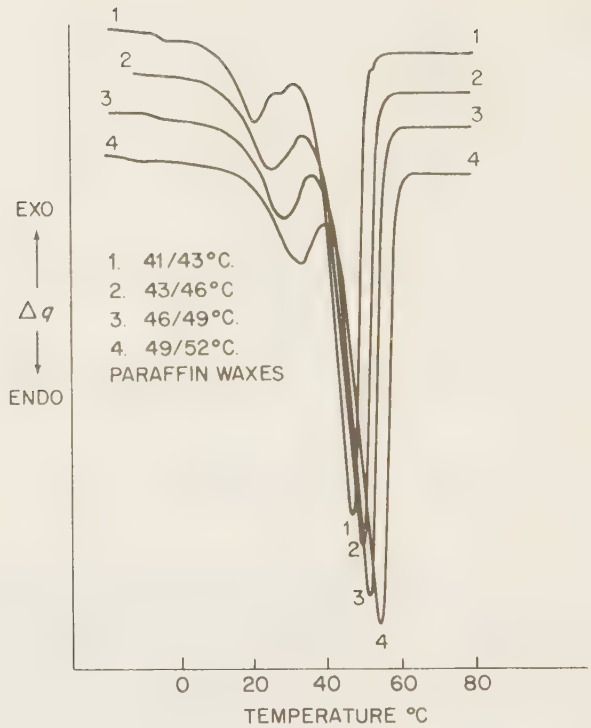

Fig. 6.

the non-normal content hinders the formation and growth of orthorhombic crystals, so that under a microscope the crystal structure of such a wax is extremely fine, generally appearing needle-like with many mal-crystalline masses. As the amount of softer amorphous highly branched hydrocarbon increases with increasing average molecular weight of a microwax, so the melting point decreases and the softness, viscosity, and ductility increase.

Several of the valuable analytical techniques applied to distillate waxes, such as glc and mass spectroscopy, are unable to resolve the complexities of the higher microcrystalline waxes, but both gel permeation chromatography (gpc),[21,22] and, to a greater extent, DSC, continue to provide useful information and records of the melting point distribution of the component hydrocarbons, and thus the overall performance characteristics of the specific microcrystalline wax.

Hardness, rigidity, brittleness, and low viscosity in a petroleum wax are associated primarily with its degree of crystallinity. Thus a microcrystalline wax with an appreciable content of normal alkanes of the highest molecular weight is hard, of medium viscosity, and of high melting point. Those with much higher non-normal contents are more viscous and softer, whilst those consisting almost wholly of iso-alkanes and cyclo-alkanes have appreciable flexibility, ductility, adhesiveness, and the higher viscosity of any of the petroleum waxes.

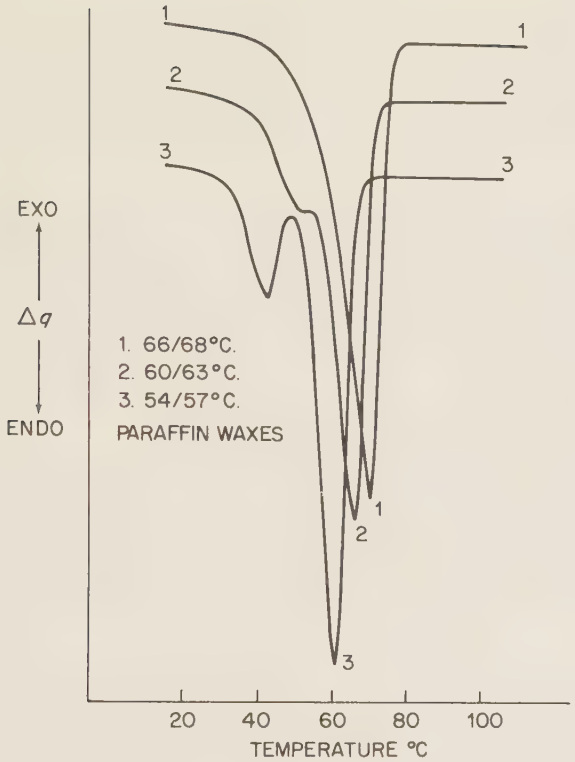

Fig. 7.

The melting point of all petroleum waxes is thus governed by the proportions and molecular weights of the various normal alkanes present. Melting point increases with the average molecular weight of the normal alkanes present, and any side-chain branching tends to lower the overall melting point.

METHODS OF TESTING PETROLEUM WAXES

Many routine methods exist for testing wax properties and assessing petroleum waxes.[23] Most of these methods are more suitable for checking the constant quality of wax output in refineries, or on receipt at a user, than for true identification or characterization purposes. Several of these methods are equally applicable to blended products, i.e. where two or more waxes of different properties, or where additives such as polymers, resins, oils, etc. are mixed in a wax, but care should be taken to ensure that the particular test method is then really appropriate.

The most commonly used tests are as follows:

1. Melting and setting point

   (a) IP 55, ASTM D87, ISO 3841

   Molten wax is allowed to cool in a specified apparatus while the

temperature is recorded at frequent intervals, the point at which the temperature remains within a range of 0.1 °C for one minute being taken as the setting point. This is the 'cooling curve' method as depicted in Fig. 5. This method is not suitable for microcrystalline or intermediate waxes, or blends of paraffin waxes with these or any additives.

(b) IP 76, ASTM D938, ISO 2207
The congealing point of a petroleum wax or petrolatum is determined by applying a drop of molten wax to a thermometer bulb, and noting the temperature at which it congeals when the thermometer is rotated under standard cooling conditions. This method is suitable for all waxes and blends. Some anomalous results can be obtained when materials of widely differing viscosities and melting or setting points are mixed.

(c) IP 133, ASTM D127, ISO 6244
The drop melting point of wax or petrolatum is determined by recording the temperature at which a drop of the sample falls from the bulb of a thermometer when heated under standard conditions. Anomalous results are obtained on blends when materials of widely differing melting or setting points or viscosities are mixed.

2. Viscosity (IP 71, ASTM D445, ISO 3104)
The viscosity of molten petroleum wax is a measure of its normal–non-normal composition, and is important in many packaging applications. The classical U-tube kinematic viscosity method is described by this method, and is suitable for all waxes and low-viscosity blends.

For much higher viscosity blends of petroleum waxes with polymeric and resinous additives, some mechanical rotational method such as described by ASTM D2669 is desirable.

3. Oil content (IP 158, ASTM D721, ISO 2908)
This standard test method is based on dissolving the oil-containing wax in a specified solvent and cooling to an arbitrarily chosen low temperature at which the insoluble material is defined as 'wax', and the soluble portion as 'oil'. Thus 'oil' is defined only by the method used, and in particular by the arbitrarily chosen temperature at which separation of solid and liquid is effected.

There is a good deal to be said for employing this test at a temperature or temperatures higher than the stipulated minus 32 °C, since the proportion of components of a petroleum wax which are liquid or semi-solid at ambient or near ambient temperatures has a considerable bearing on the characteristics and applications of that wax.

In a distillate wax, too high an 'oil' content will give a greasy texture to the wax surface, impair its tensile strength, scuff resistance, seal strength potential, staining propensity, and colour stability.

In microcrystalline waxes, an increase in 'oil' content may bring about an increase in flexibility, but too high an 'oil' content softens the

wax unduly, gives poor temperature stability, and impairs the tensile strength and sealing potential.

Whilst the IP 158 type test remains the standard test for waxes of unknown oil content, wide line nuclear magnetic resonance (NMR) techniques calibrated by IP 158 are being used increasingly for routine control of specific refinery wax streams.

4. Penetration (ASTM D1321, ISO 3992, IP in preparation)

The needle penetration of petroleum waxes is the distance in units of 0.1 mm to which a standard needle penetrates into the sample under fixed conditions of load, time, and temperature. It is an indication of the hardness of the wax, but of doubtful value in the case of very hard waxes where the precision of the method approaches the level of the readings obtained.

If the test is carried out over a temperature range, from 15 to 50°C for example, a temperature against penetration curve can be plotted which can be a very valuable guide to the staining ('bleeding') potential of the wax or wax blend, to its temperature resistance, and hence to its performance in heat-seal and packaging applications.

The penetration of petrolatum, IP 179, ASTM D937, ISO in preparation, is determined in a similar manner to the measurement on waxes, but a metal cone is used instead of a needle.

If the petrolatum is subjected to 'working', i.e. shearing, pumping, or trowelling, the structure of the product breaks down to some extent and the product softens, giving on measurement a higher penetration figure. The original penetration will not be regained unless the petrolatum is remelted and allowed to cool. A specific test, determining the worked penetration of a grease (IP 50) may be used on a petrolatum, and subjects the sample to a standard shear treatment, whereupon the penetration is then re-measured. The difference in readings before and after such treatment is a measure of the resistance of the petrolatum to shear, and is a vitally important characteristic in many industrial applications.

In general, for a given hardness of starting material, the higher the non-normal content of the petrolatum the smaller will be the difference between worked and unworked penetrations, and thus the greater the resistance to shear.

5. Colour (IP 196, ASTM D1500, IP 17, ASTM D156)

Several methods are available for measuring colour, some of which are listed above. All are based on comparing in the molten state, by transmitted light, the colour of a column of liquid wax with that of standard coloured glasses of varying intensity and hue. All such measurements are subjective, and values obtained by the different methods cannot be correlated exactly, though approximate conversions are possible.

6. Odour and taste

The detection and measurement of these properties is highly subjective.

Waxes to be used in the food packaging industry must be free from any odour or taste which could transfer itself to the foodstuff to a degree detectable by the consumer, and whilst there is a standard odour test for petroleum waxes (IP 185, ASTM D1833), there is no recognized test for taste.

Most users of wax in the food packaging industries use their own highly specific odour and taste tests employing panels of skilled operators.

7. Tensile strength (ASTM D1320)

The tensile strength of a petroleum wax is taken as the force required to pull apart a dumb-bell shaped test piece of wax. The manner of sample preparation has a profound influence on the quality of results obtained, and it is doubtful whether any great value can be attached to the results obtained on simple petroleum waxes.

The test has become more widely used with the advent of high viscosity blends of wax, polymers, and resins (the hot melts), when the figures obtained, particularly over a range of temperatures, are taken to be indicative of the mechanical properties and stress resistance of the product.

8. Modulus of rigidity

This measure of the rheological properties of petroleum waxes has never become a generally recognized test method, in spite of its undoubted sensitivity.[24] This is no doubt due to the intricacies involved in, and the variations resulting from sample preparation, together with the fact that in practice, small amounts of selected additives can easily overcome relatively large variations in the modulus of rigidity of individual petroleum waxes.

Nevertheless, many wax users employ their own specific modulus of rigidity tests in a comparative manner, and in, for example, candle production, such results are highly significant.

9. Refractive index (ASTM D1747)

This standard test, carried out using light of a particular wavelength and wax at a specified temperature, usually 80° or 100°C, is a useful method of checking variation in composition or quality of petroleum waxes. The RI of a hydrocarbon or a mixture of hydrocarbons is dependent on the degree of crystallinity of the sample; thus a sample alkane or a low average molecular weight paraffin wax gives a low RI figure, e.g. 1.4190 at 100°C, whereas a substantially normal-alkane-free microcrystalline wax gives much higher figures, e.g. 1.4420 at 100°C.

For known components in a blend, the technique can be used to give a quantitative assessment of the composition.

TOXICITY OF PETROLEUM WAXES

In recent years legislation has been introduced in most countries to protect consumers against health hazards arising from chemical substances, including petroleum products, coming into contact with foodstuffs.

Various polycyclic aromatic hydrocarbons (PCAHs) have been shown to be carcinogenic in biological laboratory tests; hence legislation in most countries now requires that hydrocarbon waxes used in, or coming into contact with foodstuffs, shall conform to specific purity requirements, and shall be shown to be substantially free of polycyclic aromatic hydrocarbons.

In an extensive testing programme on a very large number of petroleum waxes, Shubik *et al.*[25] showed by animal feeding trials that no health hazard is present if the waxes met certain purity requirements. Based on this work, and using the same waxes Howard *et al.*[26] developed a screening test for the control of polycyclic aromatic hydrocarbons which was adopted as the standard control procedure in the US (F and DA Regulations, Section 172.886).

The method is based on an extraction of any PCAHs by dimethyl sulphoxide and, after some intermediate operations, the measurement of the ultra-violet absorption of these extracts. This method has been widely adopted, although some countries use alternative techniques for PCAH control. Germany, for example, has adopted the F and DA paragraph 172.886 test for microcrystalline waxes, but on paraffin uses an alternative nitromethane extraction/paper chromatography test, with visual comparison against a known concentration of a recognized PCAH as control.[27]

INDUSTRIAL APPLICATIONS OF PETROLEUM WAXES

Petroleum waxes find extensive use in many different branches of industry. Well over a hundred different applications are listed in the bibliography, and these by no means exhaust the range of these versatile materials.

It is increasingly difficult to obtain reliable statistics regarding total world-wide wax usage, and even more difficult to find such figures broken down into end-use data. Until 1972 the American Petroleum Institute published such data for application tonnages within the USA, but since then only very general production statistics have been available through such organizations as the Institute of Petroleum within the UK, and from the Bureau of Mines in the USA until 1978, when the Department of Energy's Information Administration took over this function.

It is valuable, therefore, to have an authoritative survey[28] of output at the end of the 1970s in the USA and an estimate of end-use markets as they then existed. This and other surveys[29] showed a consumption of wax within North America estimated in excess of 1 million tons.

The largest market is in the paper converting industry, but on the whole this is showing little growth, increases in certain areas being balanced by a slow decline in other areas. In Europe, for example, flexible packaging still represents the largest usage within the paper converting field, although in USA this has been overtaken by the growth of the wax impregnated corrugated industry.

From time to time there have been dramatic setbacks in wax usage, such as for example in the 1960s when the replacement of wax coated milk cartons by polyethylene coatings resulted in the loss in the USA of up to a third of the then existing wax market. A further setback came in the 1970s with a change to the polyethylene bagging of bread from the traditional waxed wrapper, although this change has been much less complete than was at first predicted.

These setbacks have, in time, been offset by new applications within the paper converting industry and by the expansion of other markets.

Probably the biggest boost to the increase in petroleum wax consumption within the packaging and converting industries came in the early 1960s with the introduction of the hydrocarbon-compatible ethylene-vinyl acetate copolymers (EVAs). Their ability to increase heat-sealing characteristics, flexibility and toughness of petroleum waxes quite significantly, was the foundation for the growth in heat-sealable coatings and the development of the hot-melt adhesive industry.

Whilst unmodified petroleum waxes still find varied and large scale applications, there are vastly more end uses where the requirements can only be met by modifying the physical properties of the wax through blending with other materials.

The EVAs have already been mentioned, but there are very many other polymers, including vinyl acrylate copolymers, butyl rubbers, poly iso butenes, polyethylenes of widely differing molecular weight, polypropylenes, EP and EPDM rubbers, and several thermoplastic rubbers which enhance the valuable characteristics of petroleum waxes in particular applications and outlets. Many types of resins and rosins enhance adhesion, tack, and other desirable properties of wax-based products.

Since the packaging and converting industry continues to account for perhaps 50 per cent of total refined wax output, some of the major operations responsible for this tonnage will be considered in greater detail.

PACKAGING INDUSTRY

Waxed paper

The waxing of paper or calendered paper is carried out to reduce water and water vapour permeability, and to prevent to some extent the loss of strength which paper experiences when coming into contact with water.

Waxing can be carried out using many different configurations of coating machinery,[30] but essentially the paper web is passed in a continuous strip through a bath of molten wax or wax blend, or it is allowed to pass over a roll which itself dips and revolves in a wax bath. In either case, by a system of doctoring bars or squeeze rolls, excess wax is eliminated, and the weight of applied wax controlled.

When it is desirable to have little wax on the surface of the paper, for example in paper used for wrapping foodstuffs, etc., the paper web is passed through heated finishing rolls which force the wax into the pores of the paper in a process called 'dry-waxing', the resultant paper surface being dry and apparently wax-free.

When, on the other hand, the wax is retained largely on the surface of the paper, the operation is called 'wet waxing', and this is achieved by rapidly chilling the wax film from a double-sided coating or total immersion. Maximum rate of cooling occurs when the waxed paper is passed at speed through a chilled water bath whilst the wax coating is still molten.

The minimum size of wax crystal resulting from this treatment produces maximum gloss, which together with maximum moisture vapour resistance

resulting from a continuous and uniform film of wax, gives coated papers which are used for biscuit, chocolate, and sweet outer wraps, bread wraps, carton liners, shelf papers, etc. The waxes used for these operations are of low viscosity, rarely of more than 15 cp at the operating temperatures, and are blends of paraffin waxes with additions of low molecular weight polyethylenes, EVAs, microcrystalline wax, and occasionally, resins.

Coated containers

An extension of the above techniques to thicker paper substrates, or to thin solid paper-board, leads to the production of containers for cold drinks, ice-cream, fruit juices, cheese, etc., and to the very important product range of folded cartons. These are of solid paper-board, and are supplied by paper converters to customers in the form of flat blanks, already printed and wax coated. The cartons are then filled, folded and sealed by the customer, usually a large scale food processor or packer, the contents being typically frozen foods, ice-cream, butter, bacon, pies, etc.

It is general in this type of application for the additive content of the wax to be considerably higher than previously described, with EVA copolymers, polyolefines, and 'hot tack' resins being the most commonly used.

The ever-increasing proportions of polymeric additives give higher and higher viscosities to the wax coatings, and much more sophisticated machinery is necessary to apply them at speed and in controlled thickness. Although there is no agreed viscosity demarcation line, these higher viscosity wax-polymer blends have become known as hot-melt coatings, and are designed to have good adhesion to almost any substrate. They can be tailored to be heat-sealable, and to provide excellent barriers to grease, water, water vapour, gases, and odours. They are able to withstand deep-freeze conditions, and have good gloss, gloss stability, and a high degree of scuff resistance.

Laminated cartons

A further extension of carton production is the use of petroleum wax based adhesives to produce laminated cartons, two substrates being sealed together by the setting wax. Here the waxes, predominantly microcrystalline in type, are blended with tack inducing polymers such as butyl rubber, poly iso butene, EPDM, polypropylene, etc., to give high-viscosity products which do not soak into the substrates at laminating temperatures.

The operation of laminating gives further increased water and water vapour barrier properties, increased strength or rigidity, and/or a more economic package, and typical of the contents so packaged are hygroscopic detergents and soap powders.

Miscellaneous laminations

It will be obvious that since laminating grade petroleum waxes or wax blends can be designed to adhere to virtually any surface, the scope for design of different laminates for specific end uses is unlimited.

Some examples are the aluminium foil–hot-melt coated paper composite

for wrapping soap tablets, foil–greaseproof paper lamination for butter wrapping, and the 'strike through' laminates of aluminium foil to tissue paper which utilize low-viscosity laminating grade microcrystalline waxes, capable of soaking through the tissue on application of heat to form a seal with another surface.

For details of the machinery used for these and other coating and laminating operations, for more complex coating systems, and the web threading variations, the reader is referred to the specialized literature.[31]

Wax-treated corrugated board

Probably the greatest increase in wax usage in the packaging field over the past fifteen years has been in the production of wax-treated corrugated boxes.[32]

The considerable increase in strength, water resistance, ease of stacking, and the cost savings compared with heavier gauge board, wood or plastic, are the reasons for this substantial growth. Particularly in North America, considerable tonnages of fruit, vegetables, poultry, sea-food, and meat, are conveyed in wax corrugated boxes.[33] There is also a growing market in bulk containers, pallets, etc., and a significant replacement of timber in crates and cases by wax-treated boxes.

This wax treatment can be performed in three ways, by curtain coating, partial impregnation, or saturation coating, using different qualities of wax blends, and achieving different standards of performance.

(i) *Curtain coating.* In curtain coating, the corrugated board passes at speeds of up to 150 metres per minute under a falling thin curtain of molten wax blend which deposits a continuous film on the board's surface. Both sides can be coated by running the board through the coater again.

Wax blends used here contain appreciable amounts of polymer and resinous additives, and in coating the board surface give greatly increased moisture vapour and water resistance.

Impregnation of the corrugated board does not take place, so the basic board strength is not increased.

(ii) *Partial impregnation.* A controlled amount of wax, usually about 10 per cent, is used to impregnate the board in the corrugator. A higher degree of impregnation is not possible without interfering with the effectiveness of the water-based adhesive used to bond flute to liner. Some increase in board compression strength, water resistance, and performance at high humidity is realized by this technique, but a true wet service performance is not obtained.

However, following partial impregnation on the corrugator by curtain coating as previously described, a good wet-service container can be produced.

Low-viscosity paraffin wax based blends are normally used in this application.

(iii) *Saturation waxing.* This operation involves impregnating the fluting and outer liners with wax, and there are currently three techniques in use for achieving this end. In the first the wax is sprayed into the fluting

during the passage of the board along the corrugator, whilst in the second the finished board is dipped into molten wax, and in the third the board is passed vertically beneath free-flowing cascades or weirs of molten wax. All three methods attempt to remove surplus wax and ensure uniform distribution, but there is little doubt that the immersion method is the most difficult to control and leads to erratic wax weights. The cascade process appears to be the most successful, giving a high degree of process control and a large throughput.[34]

The waxes used are generally paraffin waxes modified with small percentages of low molecular weight polyethylenes, the wax pick-up being about 45 per cent of the board weight. However, refinements in operating conditions are tending to reduce this figure to a more cost effective 30–40 per cent figure.[29]

Hot-melt adhesives

As previously indicated, the transition from a low-viscosity wax, the simplest thermoplastic, to an entirely polymeric thermoplastic system is, in terms of available blends, a gradual one.

The title of hot-melt adhesives, as distinct from heat-sealable hot-melt coatings, implies that the polymer and resin components are in the major phase, petroleum wax being in the minor, and in many cases, very much the minor phase.

In this type of product petroleum wax may be regarded as a high melting solvent for the resin and polymer components, acting to reduce the viscosity, and modify the softening point, blocking temperature and 'open time' of the adhesive.

The petroleum waxes used in hot-melt adhesives are generally high melting point microcrystalline or intermediate waxes, or blends thereof, and the main outlets for the wax containing hot-melt adhesives are in book-binding, carton and case sealing, paper spiral tube winding, carpet backing, footwear, and labelling.

For a more comprehensive list the reader is referred to the very large literature which has appeared in the past years, itself a demonstration of the considerable growth of this branch of technology.[35,36,37,38]

PETROLATUM

Mention has already been made of the production of residual slack waxes by the dewaxing of de-asphalted vacuum distillation residues of crude oil, and their subsequent refining to produce petrolatum or petroleum jelly. Such products are mixtures of microcrystalline waxes and oil, and represent high-viscosity, high shear resistance materials of long fibre and substantial texture.

Petrolatum is also often produced by blending residual slack wax or microcrystalline waxes with distillate wax or distillate slack waxes and mineral oils to produce lower viscosity products of lower shear resistance, i.e. which spread more easily and have smoother salve-like consistencies.

With still higher proportions of paraffin or intermediate waxes present, stiffer pastes are formed which readily break down under mild shear conditions

to produce fluid or semi-fluid films, ideal as bases of ointments for burn dressings, etc.

Unrefined or semi-refined products from these classes are used as technical grade petroleum jellies in the production of modelling clays, moulding compounds, anticorrosive coatings, electrical insulants, etc.

Refining of these grades produces appropriate petrolatums, varying in colour from white to yellow, complying with Pharmacopoeia requirements or national food regulations, and hence finding use in pharmaceutical and food contacting applications.

Blends of residual slack waxes with heavy extract or naphthenic oils produce high-viscosity 'green' petrolatums, widely used in heavy industrial applications such as cable impregnants, anticorrosive coatings, greases, and insulants.

RUBBER COMPOUNDING

Petroleum waxes are used extensively in the rubber industry to reduce or prevent ozone cracking of stressed double-bonded rubber components such as tyres, belting, hose, etc.[39]

They operate by dissolving in the rubber at vulcanization temperatures, but become insoluble and incompatible as the rubber cools, whereupon the individual hydrocarbons migrate in a highly temperature dependent manner through the rubber mass to form a mobile film at the rubber surface. This acts as a protective physical barrier to ozone present in air which would otherwise attack any double-bonded stressed polymer, producing the characteristic cracking and crazing of the compound.

Paraffin and intermediate waxes are the only effective agents in this application, although residual slack waxes are sometimes used as processing aids.

The amount of wax used varies with the end use and type of compound, but is usually between 0.1 and 3 per cent of the total weight of compound.

CANDLEMAKING

The candle industry continues to be a large user of petroleum wax, with many hundreds of thousands of tons of paraffin wax being supplied annually for this application. The Third World countries consume a large proportion of the total, but all countries share in the production of utilitarian, decorative, and religious candles.

Stearic acid, high melting point microcrystalline and synthetic waxes, low molecular weight polyethylenes, and beeswax are commonly used additives, the candles being produced by dipping or moulding, but more often nowadays by compression moulding or extrusion.

POLISHES

Polishes for wood, leather, linoleum, and automobile bodies, etc., have traditionally contained a mixture of animal and vegetable waxes such as beeswax or carnauba, with proportions of cheaper petroleum or oxidized petroleum waxes. For ease of spreading, the waxes are dispersed in either volatile organic solvents as liquid or paste polishes, or in aqueous dispersions as cream or emulsion polishes.

With the continuing growth of synthetic polymer-based polishes, this is a relatively small and declining wax market.

WAX EMULSIONS

Where ease of application at low temperature is a requirement, petroleum waxes are supplied and used as dispersions in water. The standard production method is to mix molten wax and hot water containing emulsifying wax, using controlled cooling and homogenization to control particle size and viscosity. At the point of manufacture a true emulsion may be formed, but during cooling the wax droplets solidify; thus the final product is more correctly described as an aqueous dispersion.

The solids content commonly varies 30 to 65 per cent, of which 25 to 60 per cent may be wax. If required, other materials may be co-dispersed or emulsified, or the finished wax dispersion may be blended with compatible emulsions of modifiers such as polymers, resins, rosins, etc.

Wax dispersions find their main outlets in the particle board manufacturing industry, where their incorporation into the board improves the water repellency and dimensional stability dramatically. Other important applications are in paper and paper board production where water repellency and the qualities of clay coatings are improved, and in latex foam carpet backing formulations where surface tack is eliminated.

The applications listed above represent the major outlets for petroleum wax in industry, but significant tonnages of waxes are used in a wide variety of other applications, ranging from chewing gum and crayons, PVC lubricants and matches, pottery and ski coatings, to textiles and thermostats.

For details of these, and the very large number of specialized test methods and operations designed to assess the functional efficiency of the waxes or wax blends used in all these commercial applications, the reader is referred to the extensive specialized literature.

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Bitumens

By E. H. CHIPPERFIELD and F. D. HARPER

BITUMENS* are highly viscous liquids or solids at normal temperatures and exhibit thermoplastic behaviour—softening when heated, becoming mobile liquids on further heating and returning to their original state on cooling. They are strong adhesives and, because they are essentially hydrocarbons, are excellent waterproofing agents. Bitumens are also non-volatile and highly resistant to oxidation and weathering processes. They are, therefore, very durable. Bitumens are black or black-brown in colour, and almost completely soluble in solvents such as benzene, trichloroethylene, and carbon disulphide.

It is estimated that about 70 million tonnes of bitumen are now being used in the world annually. All but a very small fraction of this quantity is derived from the refinery processing of crude oils. Bitumen production represents an offtake of 2–3 per cent only of the total range of oil products in use in modern society.

The predominant use for bitumens is found in road construction. There are, however, many industrial applications of bitumens ranging from waterproofing materials, corrosion protectives to electrical uses.

DEFINITIONS

Natural Products

Whilst large-scale use of bitumens is a relatively modern development, bitumens have been known from the days of early civilizations. These bitumens formed naturally, when crude oils were forced through the earth's crust. Volatile components—gasolines, kerosines—were lost, leaving in some cases deposits of bitumen or in others, bitumens mixed with inorganic mineral matter. Contamination with organic matter also occurred.

Bitumen mixed with mineral matter is defined as an *asphalt*, and most applications in early times, involving bitumen, were utilizing natural asphalts. Examples are found in the Middle East of asphalts being employed to waterproof boats, as cementing agents for stone walls, and even as preservatives in the mummification of bodies.

Trinidad Lake Asphalt

This is the most extensively used and most well known type of natural asphalt today, and comes from the 'lake' in Trinidad, originally discovered by Columbus in 1498. The lake asphalt extracted from this source, after melting to drive off water, is composed of 54 per cent bitumen, 37 per cent mineral matter and 9 per cent organic matter. This product is referred to as refined lake asphalt or *Trinidad Épuré*, and because of its hard nature, is used in combination with a flux oil or a soft bitumen.

* In American terminology, bitumen is referred to as asphalt.

Rock Asphalts

In some countries limited amounts of bitumen have been found to have intruded into porous rocks such as limestones and sandstones, giving asphalts. Such deposits occur in France, Sicily, and Switzerland. They are mined or quarried and pulverized for use. Rock asphalts contain up to 12 per cent weight of bitumen. They were the earliest materials used for road paving in France in the early nineteenth century. This was conducted by heating the pulverized rock asphalt and then compacting in layers on site. Only small quantities of rock asphalts are used today and these in conjunction with flux oils or bitumens.

Petroleum Bitumens

Four distinct classes of bitumens are manufactured from crude oils by modern refinery processing. These are generally defined on the basis of three characteristics: the *penetration*, the *softening point*, and *viscosity*. In the penetration test the distance in tenths of a millimetre is measured that a standard needle, with a total load of 100 g, will penetrate into a specially prepared sample of bitumen controlled at 25°C (Fig. 1). The *softening point* (R & B) test measures the temperature in °C at which a standard disc of bitumen confined in a metal ring softens to such an extent, when heated at a rate of 5 °C min, that it deforms under the loading imposed by a small steel ball which falls a distance of 2.54 cm (Fig. 2). Both penetration and softening points are measures of consistency for bitumens.

Viscosity can also be used to define different grades of bitumens, but is more commonly applied to low-viscosity products.

The penetration at 25°C and the softening point, or alternatively penetrations at two different temperatures, can be used to define the extent to which the consistency of a bitumen changes with temperature. This is an important characteristic for bitumens, and determines the type of bitumen used for a particular application. Various factors have been used to define temperature dependence—the ratio of penetration values at 25°C and 10°C—the ratio of penetration values at 25°C (100 g 5 s) *and* 0°C (200 g 60 s), and

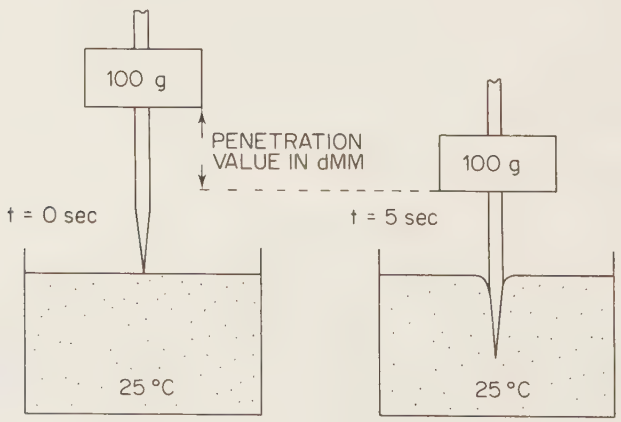

Fig. 1. Penetration test.

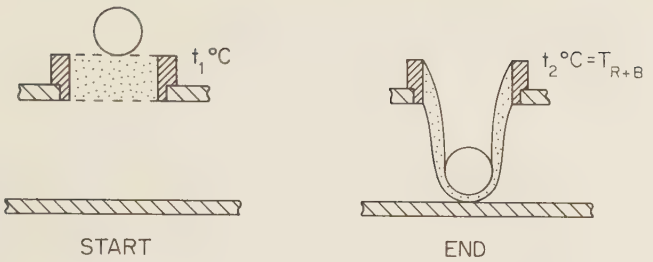

FIG. 2. Ring and ball test (softening point).

many others. The most commonly used factor, however, is the *Penetration Index* (PI), which is defined as follows:

$$\frac{\log 800 - \log (\text{PEN } 25\,^{\circ}\text{C})}{T_{R\,\&\,B} - 25} = \left(\frac{20 - \text{PI}}{10 + \text{PI}}\right) \cdot \frac{1}{50}$$

where $T_{R\,\&\,B}$ is the ring and ball softening point of the bitumen in °C. The penetration of a bitumen at the softening point temperature is about 800. The equation was developed by Pfeiffer and Van Dorrmaal[1] from the straight-line relationships found for the logarithm of penetration when plotted against temperature and also by taking the PI of a standard bitumen as having a value of 0. Bitumens more affected by temperature change have minus values and those less affected by temperature change positive values. PIs for different bitumens can be determined from the PI nomograph (Fig. 3).

Penetration bitumens. Grades of bitumen in this class are defined by upper and lower limits for the penetration test. For instance, a nominal 200 pen bitumen may have the range in a typical specification of 170 to 230 for the penetration value. Grades for these products ranging from 15 pen to 450 pen are commonly met. Whilst these materials are designated on the basis of penetration, they possess specific ranges of softening point corresponding with the range of penetration specified. PI values range from -1 to $+1$.

Oxidized bitumens. These bitumens are designated using both penetration and softening point. For example, a common grade 85/25 is named using the mean of the allowable softening point range, 85 for 80 to 90°C, and secondly the mean of the allowable penetration range, 25 for 20 to 30 penetration. Likewise 105/35 would allow the softening point to be between 100 and 110°C and the penetration value to be between 30 and 40. Bitumens of this type have a very low temperature dependence having PIs of $+2$ to $+8$.

Hard bitumens. These have a penetration of less than 15 and are designated by the prefix H and the softening point limit range, e.g. H80/90, H100/120. Whilst only the softening point is used in the grade nomenclature, each grade has a recognized range for penetration. The PI values vary from 0 to $+2$.

Cutback bitumen. The various bitumen grades given above can be fluxed with different solvents, usually petroleum distillates (white spirit, kerosine, gas oil), to reduce their viscosity and render them more easy to handle and suitable for particular applications. Grades of cutback are commonly designated by the use of values in seconds for a given quantity of the product to flow through an orifice at a fixed temperature. This is a simple viscosity measurement, and

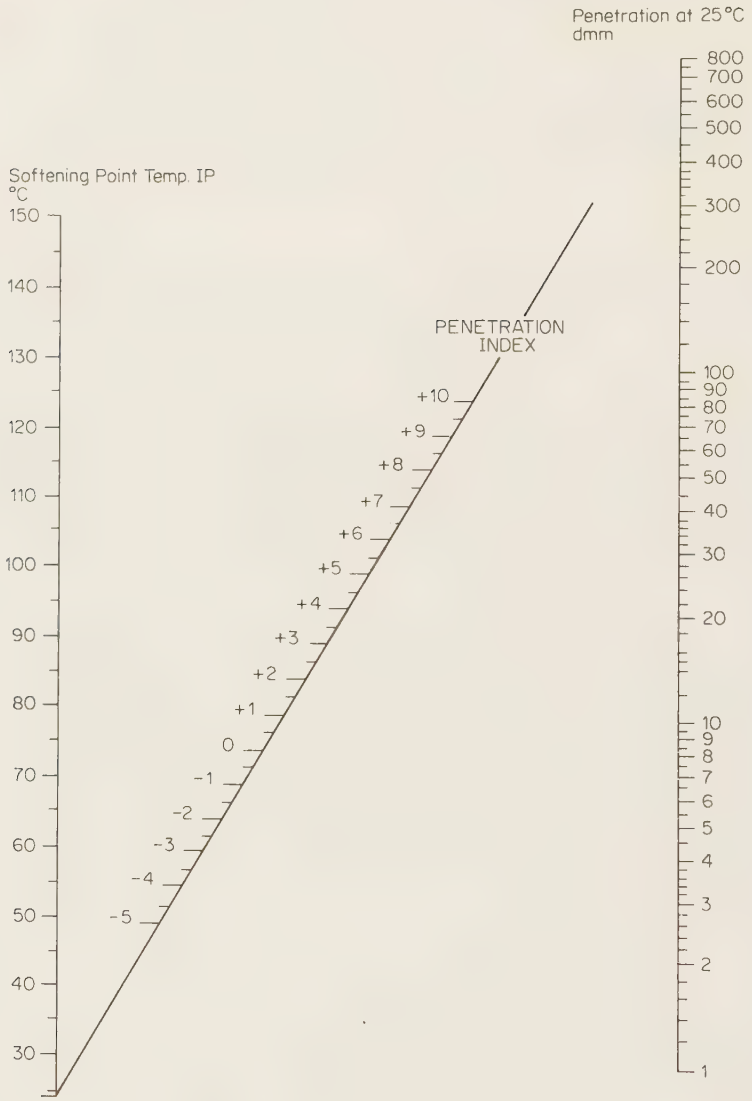

FIG. 3. Nomograph for penetration index (s.p.t./pen. 25°C).

typical products used in road applications are designated by the mid-points of the viscosity limits. The Standard Tar Viscometer is widely used with a cup having an orifice of 4 mm.

BITUMEN MANUFACTURE

Bitumens today are manufactured from carefully selected crude oils using a number of refining techniques. As described in previous chapters, a number of common oil products, motor fuels, kerosines, and light heating oils are derived from distilling crude oils at 300–350°C at atmospheric pressure.

Vacuum Distillation

The remaining fraction of the crude oil, which does not distil under these conditions, *atmospheric residue*, can be further separated into distillate products (vacuum gas oil, waxy distillates for lubricating oil manufacture) and a residue by distillation under reduced pressure, 50 to 100 mmHg, at 350–410°C. The residue from this process, *vacuum residue*, is the starting point for bitumen production. The adoption of vacuum distillation prevents thermal cracking of the components of the atmospheric residue. The presence of cracked components in bitumens has been found to affect adversely the durability of these products. Injection of steam into the residue during vacuum distillation is sometimes employed to improve the degree of fractionation between distillate and vacuum residue. This is known as *steam stripping*.

Crude Oil Selection

Crude oils for bitumen manufacture are generally chosen because they yield an adequate amount of vacuum residue, more than 20 per cent weight, and the residue has the required properties for further processing to give a full range of bitumens. Light crude oils give low-viscosity vacuum residues, which may be waxy. Whilst these can, by additional refining or the use of added components, be modified and employed to produce bitumens, it is not generally economic to do this. Very heavy crude oils are found yielding more than 50 per cent weight of vacuum residue. These are very viscous and difficult to move in pipelines. They are, therefore, used in coastal refineries and particularly by specialist bitumen manufacturers.

In this connection it should be noted that vacuum residue production in most refineries is much greater than that required to meet the volume demand for bitumens. Large volumes of vacuum residues, both suitable and unsuitable for bitumen production, are blended with other oil components to produce heavy fuel oils. It will be appreciated that the advantages to refiners in producing bitumens will be found from comparison of the use of vacuum residues as components for fuel oil with the need to add distillate materials to reduce viscosity, and the extra processing required to convert vacuum residues to a range of sales grade bitumens. Vacuum residues with high sulphur contents, greater than 4 per cent weight, may not be acceptable for conversion to fuel oil, because of sulphur restrictions on these products, but bitumens containing this level or greater of sulphur have been found to be satisfactory in

use. Bitumen production affords a means of sulphur disposal, although this is limited by market volume requirements. A further point of interest is the seasonal effect on the bitumen market met in different countries. The major proportion of bitumens being used in road construction is required in the warmer months of the year. There will be a decline in requirements in the winter, when fuel oil demand is greatest. Crude oils made available to refineries have to be processed to take account of the variation in products required and the capabilities of processing units.

Penetration Bitumens

Vacuum residues from some crude oils are soft penetration bitumens satisfactory for various applications without further treatment. In the case of many vacuum residues, however, further processing is needed to yield harder penetration bitumens having desirable mechanical properties. This is generally achieved by *air-blowing*. In this process vacuum residue at temperatures typically from 220°C to 280°C is passed into a blowing tower where compressed air is injected into the feedstock (Fig. 4). This dehydrogenates the residue (oxidation). Careful control of temperature and feed rates is necessary since the reaction is exothermic. Limited air blowing is termed *air rectification* (partial blowing or semi-blowing are less satisfactory terms). This is a much less intensive process in terms of time and air utilisation, than that used to produce oxidized bitumens.

Oxidized Bitumens

Oxidized bitumens are produced by vigorous air-blowing of vacuum residues alone or as mixtures of these with atmospheric residue, lubricating oil (waxy)

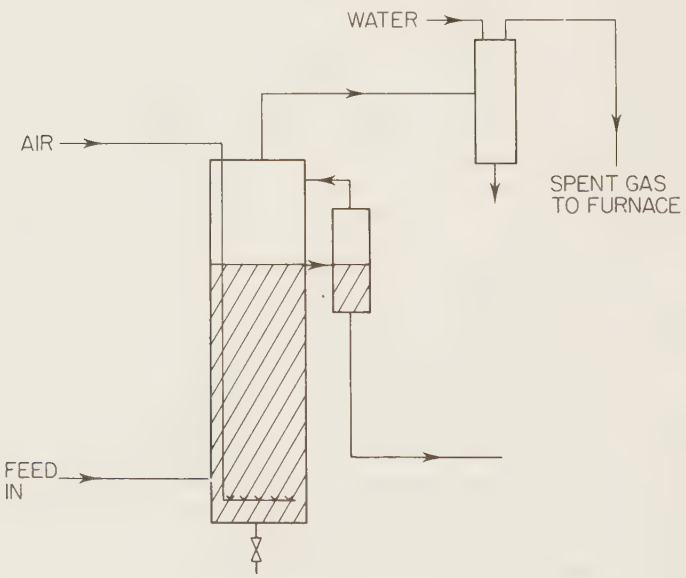

Fig. 4. Bitumen blowing unit.

distillates, or lubricating oil extracts. In a limited number of refineries catalysts such as ferric chloride (0.2 to 1.0 per cent weight) are employed to reduce the time needed for blowing. The products are referred to as *catalytic bitumens*. Small additions of other compounds (e.g. phosphorus pentoxide) can give markedly different products from those obtained by normal blowing.

In blowing processes noxious fumes are produced. These are dealt with by water scrubbing and are incinerated in a fume disposal furnace. Whilst blowing towers are used for the continuous blowing of large quantities of bitumen, for lesser tonnage speciality grades small batch blowers, 10 to 50 MT capacity, are employed.

Hard Grade Bitumens

Hard and brittle grades of bitumen can be produced by extended vacuum distillation. In some cases a very limited blowing is effected, after such distillation, to obtain the very low penetration products required.

Cutback Bitumens

Penetration, or other types of bitumens, are blended together with a controlled amount of a petroleum distillate or other solvent. Typical products for road use are obtained by mixing 100 pen bitumen with kerosine. The viscosity can be controlled and also the volatility of the solvent, which governs its loss from the cutback and a gradual return of the product after use to properties approaching those of the parent bitumens.

Blending

In refinery production blending plays an important role in making available the wide variety of bitumens which may be required. Blending can be effected by simple tank operations where measured proportions of different bitumens, or bitumens and solvents, are stirred together to produce specific products. In many cases, nowadays, refineries are equipped to conduct *in-line blending*. This enables bitumens or cutbacks to be blended in-line using highly accurate electronic proportioning equipment, and loaded directly into delivery vehicles. From storage tanks of a hard and a soft penetration bitumen, it is therefore possible to make a full range of intermediate grades as required. The blending of bitumens is governed by the relationship as follows:

$$\log P = a \log A + (1 - a) \log B$$

where P is the penetration value for the blend, a the proportion of bitumen of penetration value A, and $(1 - a)$ the proportion of bitumen of penetration value B. This type of relationship is also found for predicting the softening point values of bitumen blends. It is only accurate when similar penetration bitumens, or similar oxidized grades, are being blended. It should be treated with caution when blending products from mixtures of penetration and oxidized bitumens. Whilst in a similar way the final properties of adding heavy flux oils to bitumens can be calculated, it is much more satisfactory to conduct laboratory testing to determine blending proportions required. In controlling refinery blending operations highly accurate blending charts are used. Approximate blending properties can be found using the diagram given in Fig. 5.

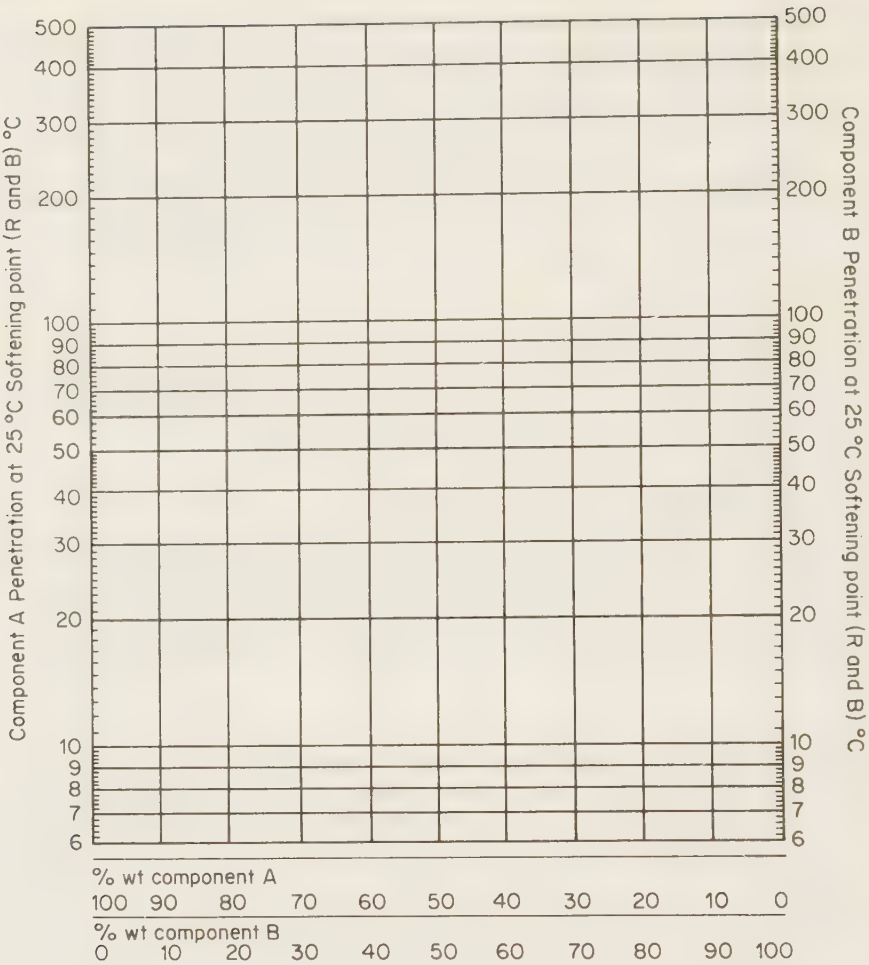

FIG. 5. Bitumen blending chart. To operate the chart a straight line is drawn, or a straight edge is laid, between the penetration of component A on the scale on the left-hand side to the penetration of component B on the right-hand scale. The penetration of the blend can be read off according to the proportion of the components shown on the bottom scale. Softening points can be substituted for penetration using the same scales.

Typical Refinery Production Scheme

A typical outline refinery production scheme for bitumens is shown in Fig. 6. The use of in-line blending limits the number of storage tanks required for producing a full range of bitumens. In Fig. 7 it can be seen how the two major processes of distillation and blowing, coupled with the addition of flux oils allow the many different grades of bitumen to be manufactured, which are required for the wide range of uses.

Handling and Distribution

Because of their high viscosities at ambient temperatures the majority of bitumens need to be heated before they can be conveniently handled. In

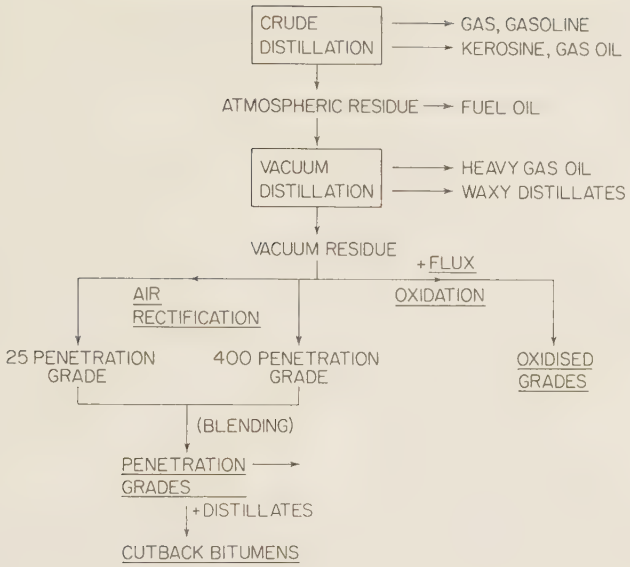

Fig. 6. Refinery schemes for bitumen production.

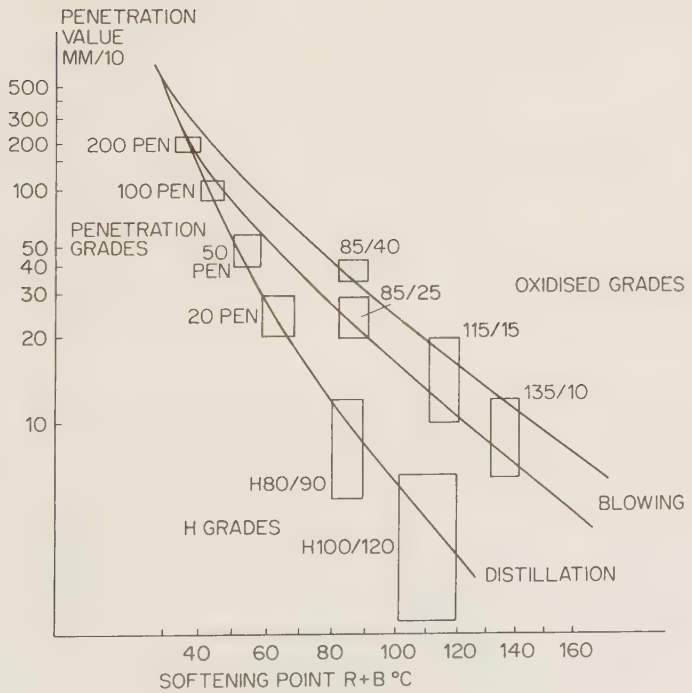

Fig. 7. Bitumen production. Different grades using distillation and blowing.

refineries, bitumens, which are supplied in appreciable volume, are stored at elevated temperatures, so that when transported to customers they can be rapidly used. In various operations associated with different applications, the following viscosity limits must be met:

Maximum viscosity for *pumping*	2000 cSt
Viscosity for *mixing* processes	150 to 300 cSt
Viscosity for *spraying*	50 to 200 cSt

In Fig. 8 a guide to *handling temperatures* for bitumens and cutbacks is given.

In nearly all countries using bitumens, nowadays bulk supplies are distributed by road tankers and/or rail tank cars at temperatures convenient for use. Road tankers are generally of 12 to 20 MT capacity, although in North

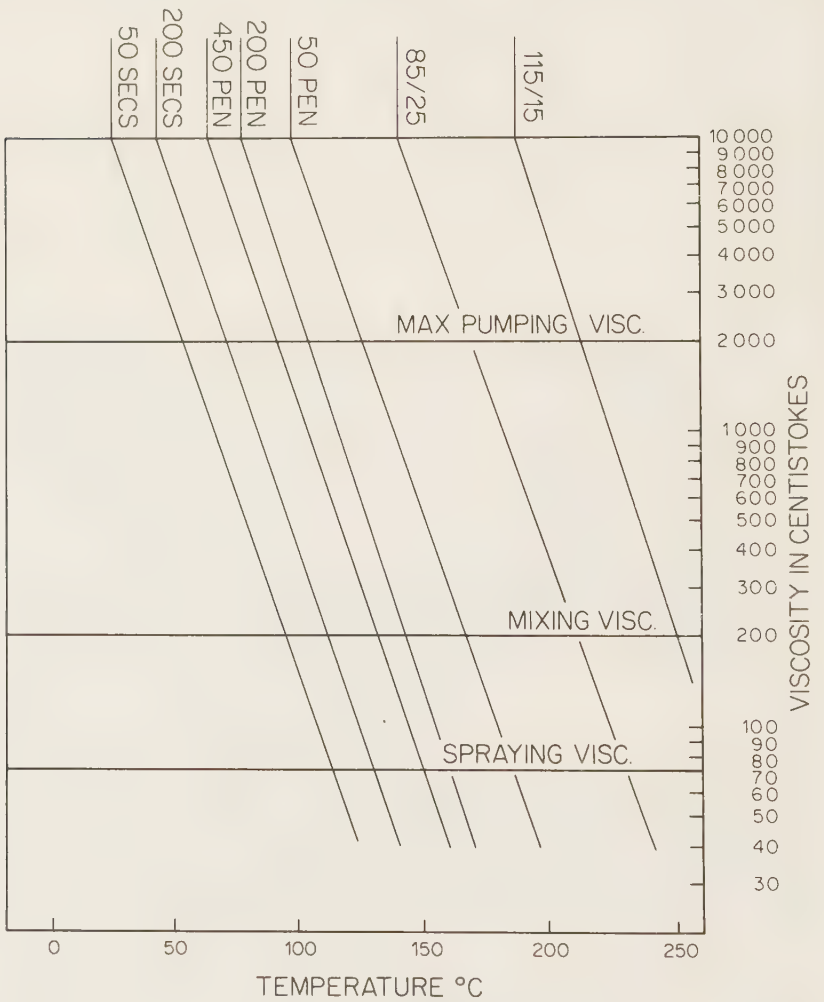

Fig. 8. Guide to bitumen handling temperatures.

America vehicles carrying up to 35 MT are found. They have insulated tanks, and whilst a fall in temperature of bitumen up to 10°C on loading may be experienced, a loss of between 1 and 2°C/h only occurs during transit. In most areas distances up to 150 km only from refineries are covered, but in some instances bitumen is being supplied over distances of 600 km. Tankers are usually loaded by pumps or gravity, and discharged by pressure or pumping. Heating equipment is sometimes fitted to tankers. Steam coils may be used in the vehicles, requiring coupling to a steam supply at the destination, or more conveniently self-contained oil or gas burning heaters are employed. Transport of bitumen in bulk by sea also occurs in some parts of the world, using specially designed vessels fitted with heated tanks. Cargoes can then be readily discharged into storage tanks on arrival at coastal installations. Where only small amounts of bitumens are required, penetration and cutbacks are supplied in drums, and oxidized and hard grades can be obtained in drums, blocks, paper sacks, and fibre drums.

Safety

With increasing customer and user concern about product safety, and more demanding legislation, it is appropriate to discuss safety aspects of bitumen. As mentioned previously, bitumen is normally handled, distributed, and used as a hot liquid. The major safety hazards are concerned with this fact, particularly the possibility of skin burns through contact with the hot product. Other potential hazards concern the flammable nature of bitumen, or bitumen mixtures, if sufficiently hot and air is present. This is particularly the case with cutback bitumens, which are normally handled above their flash point, unlike penetration grades. Inhalation of the vapours from bitumen must be avoided. Hydrogen sulphide, an acutely toxic gas, has been detected in concentrations up to several hundred ppm in tank vapour spaces above heated bitumen in certain circumstances.

Although there are few published papers on the toxicology of bitumens, it is possible to conclude that bitumens are of a low order of acute toxicity. This is confirmed by the low level of polycyclic aromatics.[2]

An extensive review of health aspects in the handling and use of bitumen and its derivatives is given in a CONCAWE report,[3] while the Institute of Petroleum Bitumen Safety Code[4] is a general guide to safe practice in the manufacture, storage, distribution, and use of bitumen.

BITUMEN PROPERTIES AND TESTING

Bitumens possess strongly adhesive and waterproofing properties. Long-term durability of bitumens is good; they are resistant to oxidation at ambient conditions, and their mechanical properties change only slowly with time.

Some penetration grades, particularly soft grades, possess high ductility, whereas oxidized grades with a greater degree of internal structure have lower ductilities. At low temperatures, penetration grades become brittle, whilst oxidized grades are less temperature susceptible.

Bitumens are almost completely soluble in carbon disulphide, benzene and chlorinated hydrocarbons such as carbon tetrachloride or trichloroethylene.

The thermal properties of bitumens are reasonably constant for different

bitumens. Of note is the low thermal conductivity which causes problems in the heating of bitumen, and limits the rate at which this process can be carried out. Overheating causes cracking and coking in hot storage. The specific heat of bitumen varies from 0.4 to 0.6 cal/g °C for the temperature range 0 to 300 °C and typical thermal conductivity is 0.14 kcal/m °C/h for normal working temperatures.

Bitumens possess very good electrical properties, having low electrical conductivity and high breakdown voltages. They are used as insulators, although traces of impurities may drastically change these properties adversely.

Bitumen specifications are built up based on a number of standard tests. Many of these tests are empirical in nature, and are not, therefore, directly related to the conditions experienced by the bitumens in use. A number of standardization bodies have published bitumen test methods, the most important being the Institute of Petroleum (IP),[5] British Standards Institution (BSI), and the American Society for Testing and Materials (ASTM).[6] Although differences in testing procedures often exist between methods issued by the different bodies, giving different numerical results, there is a movement to standardize procedures, not only between the above bodies, but also other European or world-wide organizations such as ISO and RILEM. Details of methods which have been jointly adopted are given in the respective test method publications.

The penetration and softening point tests which measure consistency of bitumen have already been described. Other tests which are commonly carried out on bitumen are reviewed below, and their IP Method Numbers are given where appropriate.

Viscosity. This property of bitumens can be determined by various methods, including the use of capillary viscometers, normally at high temperatures. Viscosity is very important in connection with cutback bitumens and is measured as the time for a standard quantity of material to flow through a specified orifice under defined conditions at a fixed temperature.

Kinematic viscosity (IP 71)
Standard Tar viscosity (IP 72)

Ductility. The ductility of bitumens is measured by stretching a standard test-piece under fixed conditions until it forms a thread which subsequently breaks. The elongation at the break time is the ductility value. Normally this test is conducted at 25 °C.

Breaking point (FRAASS). This measures low-temperature brittleness by repeatedly flexing a thin film of bitumen while it is being cooled. The temperature at which cracks first show is the breaking (or brittle) point.

Breaking Point of Bitumen FRAASS Method (IP 80)

Flash point. Flash points (open or closed) of cutback bitumens are of particular importance because they contain volatile flux. Penetration and oxidized grades are normally stored and used at temperatures well below their flash point.

Flash Point (Open) and Fire Point (Pensky Martens) (IP 35)
Flash and Fire Points Cleveland Open Cup (IP 36)

Loss on heating. This test reflects the changes in properties of bitumens during refinery and depot handling and storage. The sample is heated under standard conditions for 5 hours and the loss in weight determined, as well as the change in properties of the residue, such as penetration.

Loss on Heating—Bitumen and Flux Oil (IP 45)

Thin film oven test. This test measures the loss of volatiles and hardening of a thin film of bitumen under standard conditions in an oven. The results correlate with the changes during the manufacture of road materials, when hot bitumen and stone are mixed and exposed to high temperatures in contact with air.

Solubility. Solubility of bitumen in a solvent is a measure of impurities present. Originally carbon disulphide was used as the solvent, but now the less hazardous trichloroethylene is normally specified.

Solubility of Bituminous Binders (IP 47)

Wax content. High wax contents of bitumens have an important effect on temperature/viscosity relationships. Two methods may be used to determine wax, either destructive distillation, or removal of asphaltic constituents by concentrated sulphuric acid, followed by solvent extraction and wax recrystallization. The latter method gives significantly higher results than the destructive distillation method. It is important to take the method used into consideration when evaluating test results.

Permittivity

In the UK, it was observed that the development and retention of texture depth or roughness over time and thus skid resistance, of rolled asphalt varied when using bitumens from different crude sources. The mechanism for this is not fully understood, but is dependent on the chemical composition of the complex components present in bitumen. In practice, it was found that the dielectric constant, or permittivity, of bitumens used, measured at 25°C, correlates with surface texture development of rolled asphalt over time.[7] A standard test to measure permittivity was developed, using either glass or metal cells.

Permittivity of Bitumen (IP 357)

BITUMEN CHEMISTRY

Bitumens are complex mixtures of very many different compounds of high molecular weight. They are generally regarded as colloidal systems[8,9,10] consisting of *asphaltene* micelles dispersed in a lower molecular weight medium termed *maltenes*. The micelles are considered to be asphaltenes together with an adsorbed covering sheath of high molecular weight aromatic resins, and such layers extend outwards into the less aromatic oily dispersion medium. As the number of micelles dispersed in the maltenes increases, the behaviour of the colloid changes from a SOL–GEL then to a GEL. The stabilized micelle only precipitates when a solvent (e.g. n-heptane) is added.

Different methods have been used to study bitumen chemistry, the most

successful being those using separation techniques to obtain broad component groups.[11,12] Whilst it is not possible to relate chemical composition directly to physical behaviour, guidelines can be found, which are useful in controlling the selection of feedstocks in refinery processing and also in selecting bitumens for particular applications.

Chromatographic techniques are employed in procedures for separating the different fractions. First, the asphaltenes are precipitated using n-heptane. It has been shown that heptane asphaltenes represent the hard core of the asphaltenes with little or no absorbed materials remaining.[13] Three other fractions may be obtained by separating the material in solution by chromatography using a silica gel/alumina column. The *saturates* fraction is obtained as a n-heptane eluate, the *cyclics* as a toluene eluate, and the *resins* as a toluene/ethanol eluate. The main characteristics of these broad chemical groups are as follows:

Asphaltenes. These are brown to black amorphous solids containing mainly carbon and hydrogen, but in addition nitrogen, sulphur, and oxygen. They are aromatic materials of high molecular weight (200–5000 No. AV MW).

Resins. These contain largely carbon and hydrogen, but also small amounts of sulphur, nitrogen, and oxygen. They are adhesive, solid or semi-solid, dark brown in colour, and very polar in nature. The typical molecular weight range is 900–1300 (No. AV MW).

Cyclics. These are viscous liquids comprising about 50 per cent of penetration bitumens. They contain largely carbon and hydrogen, but also some sulphur, nitrogen, and oxygen. Their typical molecular weight range is 550–850 (No. AV MW).

Saturates. These are solids or viscous liquids, which range from straw to white in colour. They consist substantially of hydrocarbons of molecular weight range 500–800 (No. AV MW). They can be straight-chain, branch-chain, or alkyl aromatics where the alkyl chain is long. Saturates that are solid at ambient temperatures have appreciable *wax* contents.

The composition of typical 100 penetration bitumens is shown in Fig. 9.

Relation of Chemistry to Properties

In processing bitumens the relative proportions of the four broad components can be controlled by distillation and blowing. Distillation will reduce the saturates content and at the same time increase the relative proportion of asphaltenes and resins by concentration. In contrast, air blowing, by dehydrogenation and polymerization increases the asphaltenes content with a corresponding decrease in the cyclics content. The resins content and saturates content remain substantially unchanged. The temperature dependence of bitumens is controlled mainly by (i) the concentration and nature of the asphaltenes, these being relatively inert materials, (ii) the saturates fraction which controls the degree to which a gel character may appear in the bitumen colloid.

The balance of the different components found in bitumens in normal use ensures they will be durable in different applications over many years. Weathering processes have been found to be extremely slow, and are governed by exposure to light and the availability of air.[14] Hardening of hot bitumen in

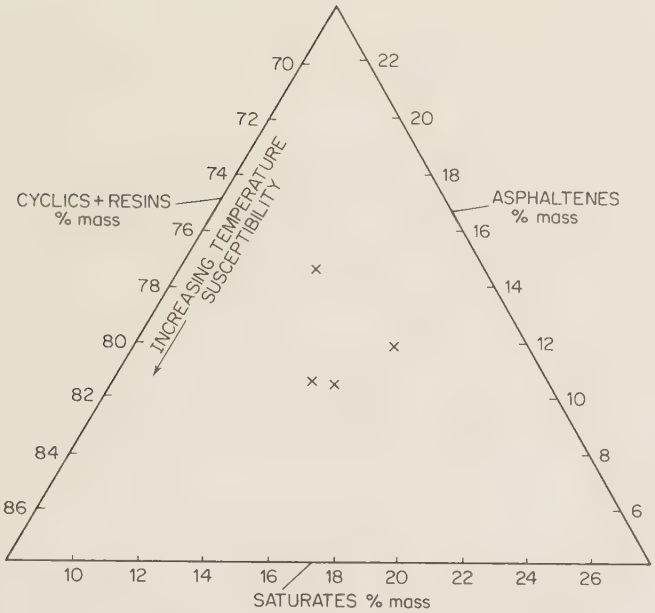

FIG. 9. Broad chemical composition. 100 penetration bitumens.

storage is controlled substantially by the loss of volatile components and care must be taken to ensure that bitumens are stored at appropriate temperatures and not overheated in manufacturing processes.

Whilst chemical composition can be related to physical properties, given a particular feedstock, it should be noted that bitumens of markedly different chemical composition can have similar physical properties, if derived from different crude oils.[15] It will therefore be appreciated that the definition of chemical component concentrations does not satisfactorily describe the nature of bitumens for specification purposes.

BITUMEN RHEOLOGY

The mechanical properties of bitumens govern the applications for which they can be used. Such characteristics are determined by the rheology of the different types of bitumen. Bitumens are *visco-elastic* materials, exhibiting a combination of viscous flow and elastic behaviour. This is dependent on the colloidal nature of the bitumen resulting from the chemical composition. Three general classes of bitumens can be recognized for normal operating temperature ranges:

(i) SOL type bitumens. These exhibit the properties of a viscous liquid (Newtonian or almost Newtonian behaviour), viscosity being virtually independent of the rate of shear. Very soft penetration grades may be in this class.

(ii) SOL-GEL type bitumens. These are slightly elastic and non-thixotropic. Under stress imposed for short periods they behave as

elastic materials, whereas if a stress, even small, is imposed continuously their viscosity becomes almost independent of the rate of shear. The majority of the penetration grades of bitumen fall into this category.

(iii) GEL type bitumens. These are strongly elastic and thixotropic. When deformed slightly they show almost complete recovery when the imposed stress is removed. They also have a yield stress. These characteristics are typical of oxidized grade bitumens.

The majority of bitumens in use, therefore, show flow properties which are completely influenced by the time of loading and also the temperature at which this occurs. At elevated temperatures, however, all bitumens are essentially Newtonian liquids.

To describe the visco-elastic behaviour of bitumens the concept of a time dependent Young's modulus has been developed which is also a function of the time of loading. Van der Poel[16] introduced the term *stiffness* to describe time dependent moduli, the stiffness being:

$$S = \frac{\text{tensile stress}}{\text{total strain}}$$

dependent on time of loading, temperature, softening point, and penetration index of a bitumen. To facilitate the calculation of stiffness a nomograph has been constructed.

At low temperatures all bitumens are found to behave elastically and have equal stiffnesses of 3×10^9 N/m^2 (3×10^{10} dynes/cm^2). The penetration of bitumen is found to correspond with a stiffness value for 0.4 second loading time.

In the numerous applications for the different grades of bitumens a wide range of shear rates, stresses, and temperatures is found. Behaviour at long loading times can be studied in conventional viscometers, but short loading times such as those representative of traffic stresses on roads have been studied by various instruments using vibrational techniques.[17,18] The effects of frequency and temperature can be separated by the reduced variable approach using the principle of time–temperature superposition. The use of temperature–frequency reduced variables[19] permits the construction of modulus frequency master curves covering several decades of frequency. In recent years a model for bitumens has been available, which enables master curves to be established from only a few measurements.[20] The behaviour of bitumens so defined can be extended to describe the behaviour of bitumens in mixtures with mineral aggregates or fillers.

BITUMEN SPECIFICATIONS

A wide variety of tests, including those described above, are used in national bitumen specifications around the world. As many of the tests are empirical, they do not directly relate to the conditions experienced by bitumens in service. Bitumen manufacturers, therefore, normally carry out many more tests than are required by the national specifications to ensure that their products are

suitable for intended end-uses. This includes full-scale road trials where appropriate for road bitumens.

In the UK, the three parts of British Standard 3690: 1982, specify bitumens for road use, industrial use, and bitumen mixtures (with Trinidad Lake Asphalt, Coal Tar, etc.). Penetration and softening point are used to classify penetration, oxidized grades, and bitumen mixtures.

Much attention has been given over the years to the correlation of laboratory testing and the field performance of bitumens, and the development of specifications involving the fundamental properties of bitumens which govern their behaviour in practice. In view of the widely different national specifications in current use, rationalization as well as improvement is obviously desirable. Suggestions for satisfactory specifications have been made,[21] but achievement based on fundamental measurements is still a long way off. A change has been made in the USA away from penetration grading to viscosity grading for paving grade bitumens, using viscosities at 60°C and 135°C instead of penetration and softening point. This has so far not been followed in the UK.

One fact which is often overlooked in specifications is the hardening of bitumen during the mixing operation, and the consequent fact that the chemical and physical properties of bitumen in use differ appreciably from those of the initial bitumen. It may, therefore, be more realistic to base bitumen specifications in the future on properties after ageing in the laboratory, to reproduce the changes occurring in the mixing process.

BITUMEN APPLICATIONS

The inherent properties of bitumen, its relatively low cost and ready availability have led to its extensive use in a wide range of applications. Road construction and maintenance are the major outlet, taking approximately 90 per cent of total bitumen production in the UK. Other uses are in different engineering fields, and for many industrial purposes.

Road Uses

Bitumen is used as a strong durable binder giving desirable mechanical properties to various mixtures with mineral aggregate in road construction. Mostly these have been used in the surface layer or layers to seal the road structure, maintain its strength in the prevailing climatic conditions, provide strength to support traffic loadings and a good, dust-free and skid-resistant riding surface.

Roads constructed using bitumen are referred to as 'Flexible Roads'. They are constructed of layers of different materials increasing in strength from the sub-grade to the surface, so that the load imposed by vehicles is distributed by the total structure and can thus be supported by the sub-base without deformation (Fig. 10). Asphalt surfacings render the construction resistant to water ingress, preserving the strength of the sub-grade. Underlying layers may be built with unbound crushed stone, but there is increasing use of asphalt mixes for these also, to give better mechanical properties, with constructional advantages. Several pavement design methods have been developed to

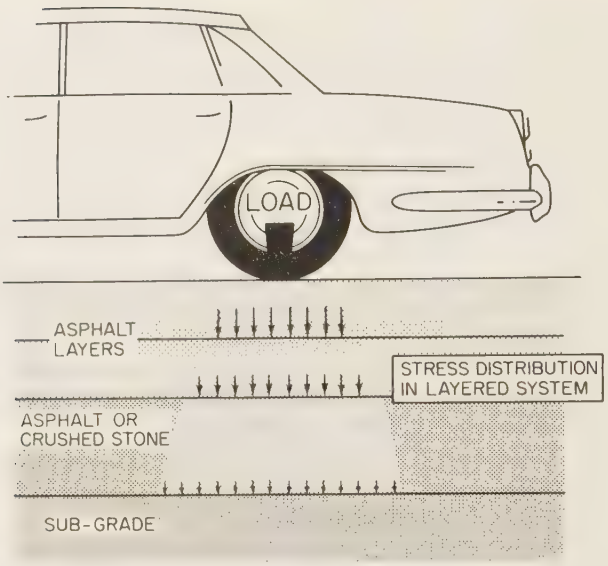

FIG. 10. Load distribution on a flexible road.

determine the thicknesses of the various layers, depending on the predicted traffic loading, climatic conditions, nature of the sub-grade, and available stone material.

Flexible roads form the majority of road networks world-wide, because of the variation in pavement designs possible to suit all classes of traffic, from light to heavy, and all climatic conditions.

There are several general types of surfacing mixtures used, differentiated by composition and to some extent function, and subject to variations and differing nomenclature in different countries.

(a) *Rolled asphalt* is used extensively in the UK to surface the most heavily trafficked roads. It is a gap-graded mixture in which sand, filler, and bitumen are present as a dense mortar between coarse aggregate (rock, gravel, or slag).[22] About 7.5 per cent wt relatively hard penetration grade bitumen (35–70 pen) is used to give the necessary mechanical strength and stability to the material. It is pre-mixed, transported, laid, and compacted hot. In order to achieve a rugous texture and high skid-resistant surface, single-size chippings pre-coated with bitumen are rolled into the surface. To preserve this texture over time, only selected bitumens having a minimum specified permittivity level may be used in the UK.

(b) *Asphaltic concrete* is used in many countries for surfacing heavy duty roads. It is manufactured by blending coarse and fine crushed stone and filler into a continuously graded mixture to provide an interlocking system of stone with a particular voids content. Penetration grade bitumens (50–100 pen) are added (5/7% wt) to fill about 80 per cent of these voids, making the mixture impermeable,

FIG. 11. Road materials mixing plant.

with high density on compaction, for surfacing use. As with rolled asphalt, the mixture is made, laid, and compacted hot, the temperature depending on the grade of bitumen used.

(c) *Bitumen macadam* is used for surfacing minor or less heavily trafficked roads. It contains a continuously graded aggregate coated with 4/5% wt of bitumen (100 pen of softer) or a cutback bitumen. Because of the high proportion of large stone in its formulation, the finished compacted material has an appreciable porosity, or open texture.[23]

(d) *Surface dressing* is a widely used form of surfacing to seal and maintain road structures. It consists of spraying a thin film of hot bitumen (usually cutback) or bitumen emulsion on to the road surface, and covering with a layer of single-sized chippings. These are then rolled to press them into the bitumen and into contact with the original surface, so that they embed under the influence of traffic.[24]

Hydraulic Applications

Bitumen is also employed to produce waterproofing layers in hydraulic works.[25] Bitumen membranes or asphalt surfacings are used in sea-wall

FIG. 12. Road laying operation in progress.

construction, surfacing of break-waters, canal and reservoir lining, and dams. Surfacings using mixed materials involve constructional techniques similar to those used for roads, although asphalts richer in bitumen are common.

Industrial Applications

There are many industrial applications of bitumens, which can be categorized, depending on the most important feature of bitumen for a particular application.

(a) *Waterproofing.* This is the largest use for bitumens in the industrial sphere, particularly for roofing. Roofing felt manufacture is based on the use of hot penetration grade bitumen (typically 100 or 200 penetration) to impregnate by immersion a dry sheet produced from waste rag, wood pulp, or more recently glass fibre or polyester. A surface coating is then applied to both sides of the saturated felt, using an oxidized grade of bitumen (e.g. 85/40, 105/35), with sometimes a proportion of added filler. The combination of bitumens allows roofing

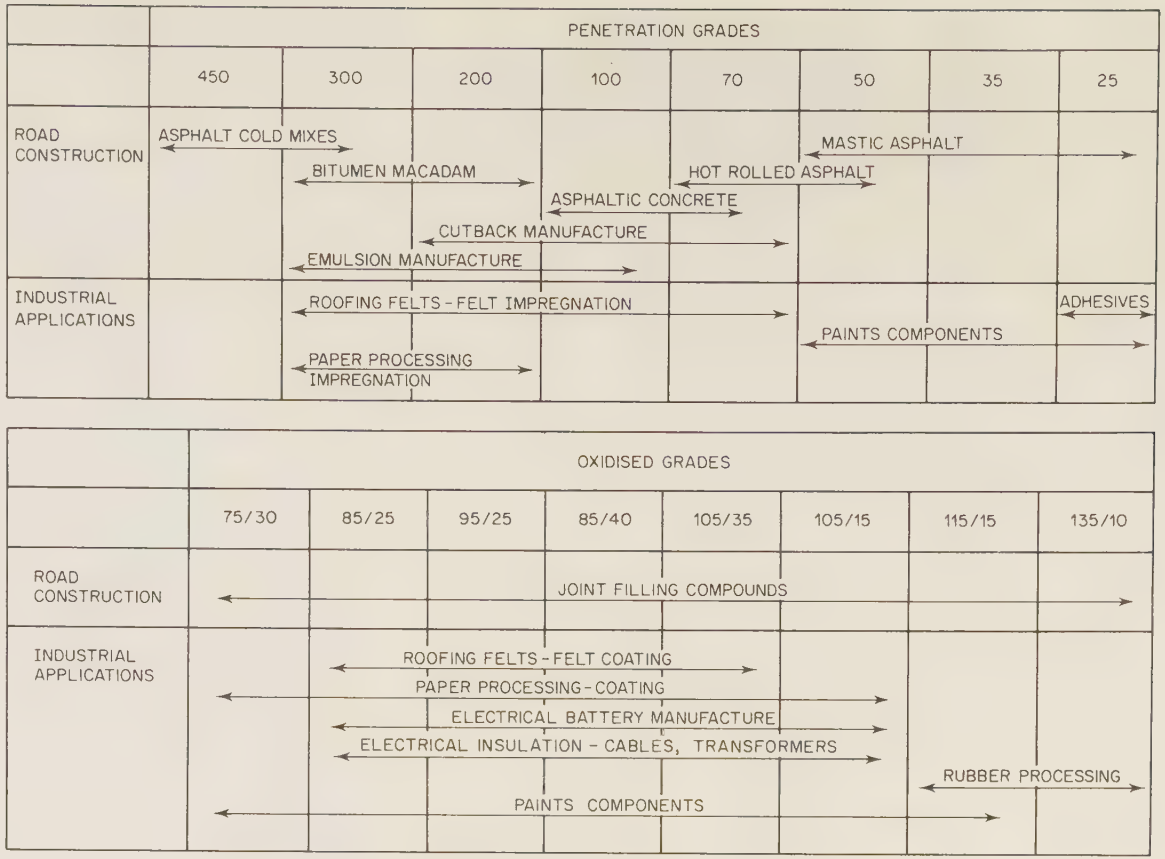

FIG. 13. Principal uses of penetration and oxidized bitumens.

felts to be rolled for storage and provides flexible characteristics in working conditions on roofs.

Impregnated felts, hessian, or glass fibre, are used as damp-proof membranes in masonry. Mastic asphalts are used to construct waterproofing membranes for flat surfaces in flooring or roofing. Mastic asphalts are composed of finely divided limestone with a high bitumen content (12–17% wt) of a hard penetration grade (15–20 pen).

Waterproof papers, consisting of paper coated or laminated with bitumen are used for packing or building purposes.

(b) *Insulation.* The insulating properties of bitumens enable them to be used for cable-jointing compounds and heavy-duty cable wrappings. Their thermal and sound insulating properties find use in the construction of cold stores, or in sound-deadening panels in cars.

(c) *Protective coatings.* Bitumen paints are produced as cutbacks or emulsions, generally using hard or oxidized bitumens. For the external protection of steel pipes, oxidized bitumen with mineral filler is used.

(d) *Joint-filler and sealants.* These are used for joints in concrete structures or sealing gaps between masonry and metal or wooden frames. They are putty-like products based on oxidized bitumens and rubber/bitumen blends, bitumen/filler compositions, and mastics.

(e) *Adhesives.* Oxidized bitumen is used as an adhesive in sticking roofing felt down, or between the layers in constructing 'built-up' felt roofing.

Other bitumen compositions find use in the fixing of polystyrene or cork slabs for insulation, or for fixing vinyl floor tiles.

Typical grades of bitumen used for the various applications are shown in Fig. 13.

MODIFIED BITUMENS

Bitumens with one or other of their properties modified for special uses, usually by blending with other compounds, have been investigated over many years, but are now finding increased usage. Properties which can be improved include temperature susceptibility, adhesion, cohesion, resistance to oils, etc.

Blends with synthetic polymers, such as styrene/butadiene/styrene co-polymer (SBS), or ethylene vinyl acetate copolymer (EVA) have found application in road surfacing[26] and in the production of single-layer felt roofing. EVA modified bitumens (5% EVA) have the property of increasing the resistance to deformation of rolled asphalt mixes by a factor of two or three over unmodified bitumens. EVA or SBS in higher proportion (10/13% wt) in bitumen gives roofing felt a higher degree of elasticity than bitumen alone.

The use of bitumen with added sulphur as a binder for road use has been extensively investigated.[27] Increased deformation resistance, and better workability of the mix result, but the environmental problems (formation of H_2S) make the mixture difficult to use.

An interesting development in the UK is the use of a 'heavy-duty' bitumen for increasing the stability of rolled asphalt mixes. This is a penetration grade bitumen with a high penetration index, i.e. high softening point for a given

penetration. Because of the higher softening point, higher working temperatures are necessary with this binder.

Bitumens mixed with epoxy resins have found applications for surface dressing in very heavy duty surfacing situations, such as at major roundabouts.

Modified bitumens have the common problem of increased price, but technical advantages can in certain circumstances outweigh this disadvantage.

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Special Products

By H. J. BEZER, P. S. DUCKWORTH, H. KNIGHT, A. E. WILLIAMS and R. J. A. WILLS

INTRODUCTION

The spiralling cost of crude oil over the past ten years has led to refiners and consumers devoting considerable effort towards more efficient processing and conservation of petroleum products. These trends are reflected in the speciality petroleum products discussed in this chapter.

For example, less naphthenic acids are available due to changes in crude sources and refining. An alternative route to medicinal white oils (via hydrogenation) is now possible, which makes better use of the crude oil. Hydraulic fluids and metallurgical oils which contain water, are becoming popular in special circumstances, and reduce the requirements for oil derivatives but require considerable expertise to develop.

Whilst trends away from petroleum products can be seen, the chapter clearly indicates that there is still no substitute for them in the majority of applications.

NAPHTHENIC ACIDS

Naphthenic acids occur in virtually all crudes in amounts ranging from traces (around 0.02 per cent wt) to commercially and technically significant quantities (2 per cent wt or even more). The naphthenic acid content of a crude is, as wt per cent, about half the acidity expressed as mg KOH/g.

Chemically, naphthenic acids are mono-carboxylic acids mainly having a ring structure with side-chains of varying length. The number of fused rings may vary from 1 to 5 and are predominantly cyclopentane, but a small fraction may be cyclohexyl; acids with polycyclic structures have also been found. The carboxyl group is seldom attached directly to a ring.

In their general behaviour the naphthenic acids exhibit many similarities with fatty acids and in fact much of their technical importance is linked with such similarity. Physically they are oily liquids, water-insoluble (except for the lowest members which are sparingly soluble) and hydrocarbon-soluble. They have a characteristic odour resulting from the phenols and sulphur compounds which are extracted with the acids.

Distribution of naphthenic acids throughout crude oil is non-uniform; there is a gradually rising concentration from about the beginning of the kerosine fraction upwards, reaching a peak in the gas oil range (*ca* 350°C) and tailing off gradually thereafter.

The naphthenic acids that are of importance to industry are obtained largely from oil fractions boiling between 200° and 370°C, but some acids are isolated from lighter kerosine cuts or from heavier lubricating oil distillates. Naphthenic acids are not generally present in straight-run gasoline, and those

in bitumen cannot normally be recovered. It is, however, possible to recover a wide range of naphthenic acids directly from crude oil in the case of the few crudes that can conveniently be neutralized prior to distillation. The resultant aqueous alkali soap solution is then 'sprung' with sulphuric acid to release the naphthenic acids, which are next themselves submitted to distillation (steam or vacuum) in order to segregate the middle range acids of high acid value and low unsaponifiables content.

Much of the acid formerly recovered by extraction before the distillates of acid components is no longer available, because modern purification procedures destroy the acids. However, when their extraction is economically viable, the naphthenic acids are isolated from the fractions in which they occur by extraction with dilute aqueous caustic soda solution. The aqueous solution may then be extracted with light naphtha to reduce the oil content of the finished naphthenic acid. The free acids are isolated by treatment with sulphuric acid, followed by air blowing to dry the acids. If specially pure and pale acids are required, the crude naphthenic acid is distilled under vacuum. Acid and earth treatment may also be used to improve colour. Alcoholic soda solutions are used in some cases to extract the acids, and methods using ammonia are also known.

Naphthenic acids are corrosive towards metals; thus precautions have to be taken in manufacture and storage; among the commoner metals lead is the most easily attacked and aluminium the least. Commercial acids, unless specially purified, are usually dark and have a characteristic odour; molecular weight is most frequently in the range of about 200–350; at the lower end of this range distillation at atmospheric pressure is possible, with a boiling point in the region of 200 °C. As the molecular weight and level of boiling range increase, the acid value falls, from 250–300 for acids from a heavy naphtha to 230–250 for those from kerosine, 170–230 for those from gas oil, 120–150 for the rather less frequently encountered acids from lube oils, whilst acids isolated from bitumen have acid values in the region of 80.

The density of the acids is somewhat greater than that of the petroleum fraction whence they are separated; a typical value for a gas oil acid of acidity say 230 would be around 0.96 g/cm^3, with viscosity higher than that of the source distillate. The product of d_{20} and n_D^{20}, which is around 1.44, has been suggested as a means of distinguishing naphthenic acids from hydrocarbons, and from other oxygen-containing compounds found in petroleum, such as aliphatic acids (*ca* 1.30) and phenols (over 1.5).

Naphthenic acids are used industrially mainly in the form of soaps, although the acids themselves are used to a certain extent in rubber as a softener to replace stearic acid, as a tack promoter, and in the regeneration of rubber. Use for the extraction of metals (e.g. rare earths) from solution has also been reported.

The chief use of sodium soaps is as emulsifiers in soluble oils and for bitumen. Sodium naphthenate finds some use in Eastern Europe as a washing soap base, some bactericidal action being claimed; it also has application in agriculture and horticulture, since it would seem to function as a fertilizer stimulator by virtue of its wetting properties. Alkali metal soaps have also found uses as emulsifiers in olefin polymerization processes. One of the largest uses of naphthenates is as paint driers, where the lead, calcium, cobalt, manganese and

zirconium soaps are mainly used; the last is finding an increasing use as a substitute for lead naphthenate in applications where freedom from toxicity is necessary. The lead soap finds extensive use as a means of imparting extreme pressure properties to lubricants, but its use is expected to decline because of concern over the toxicity of lead compounds. The calcium soap has been used in lubricants as a detergent. A further large quantity of naphthenates finds a use as fungicides and insecticides, the chief soaps used in this case being copper and zinc. Copper naphthenate has been used extensively as a rot-proofing agent for textiles and as a preservative for wood. Tin and antimony soaps have been reported to be useful in inhibiting castor oil against gumming and oxidation.

More recent developments in the use of naphthenates have been as catalysts in organic oxidation processes, and as fuel additives. Manganese and lead naphthenates are active catalysts in the oxidation of kerosine to give high molecular weight hydroxy acids, whilst cobalt naphthenate acts as a catalyst in the conversion of olefins into higher alcohols. Manganese naphthenate is also used as a catalyst in the manufacture of dicarboxylic acids from paraffin wax. Heavy metal soaps (zinc, lead, calcium, chromium) have been used as activators in the vulcanization of rubber. It is claimed that formation of sediments and deposits in diesel fuels and heavy fuel oils can be prevented by the addition of iron, manganese and cobalt naphthenates, and it is also claimed that addition of a mixture of these soaps promotes combustion of fuel oil. Calcium naphthenate can be used as a motor oil additive. Cobalt naphthenate has been employed in conjunction with peroxide catalysts to accelerate the curing of unsaturated polyester resins in the building of glass fibre laminates.

A further use of naphthenate soaps is as corrosion inhibitors in rust-preventive oils. Their surface-active properties, resulting from their polar/non-polar nature, cause them to be absorbed on metal surfaces, forming closely packed molecular layers; naphthenates of aliphatic amines of chain length C_8 to C_{15} have been reported to be satisfactory components of corrosion-inhibiting oils.

Organic derivatives of naphthenic acids also find other applications, for example, esters as plasticizers, amides as aids in dyeing, and amines as flotation agents for ores.

PROCESS OILS

A considerable volume of oil fractions is used in admixtures with a wide range of other non-oil derivatives as extenders, viscosity modifiers, solvents, etc. The term 'process oils' encompasses oils which are used in this way.

Manufacture

Lubricating oil distillates are split by solvent extraction processes, the main objective being to concentrate the hydrocarbon molecules which have superior lubricating properties. This fraction, the raffinate, contains a high proportion of saturated hydrocarbons suitable as lubricants. The other fraction, the extract, is a concentration of the more aromatic and polar molecules. The ratio of the types of molecules concentrated into the two fractions is controlled by the choice of solvent and its ability to preferentially solubilize the aromatic and

polar molecules. Solvents include sulphur dioxide, phenol, furfural, sulfolane, n-methylpyrrolidine, which are later removed and recycled.

For use as process oils the two fractions can best be distinguished as high and low solvency grades.

High Solvency Process Oils

The high solvency oils without extra modification or treatment have a dark colour due to their sensitivity to oxidation and the presence of highly condensed aryl/heterocyclic molecules. Their viscosities range between 15 and 2000 cSt at 40°C, depending upon the viscosity and nature of the original distillate. The proportion of the distillate extracted can be between 10 per cent and 60 per cent, the exact amount being a design parameter of the process. The smaller the proportion of distillate extracted the more aromatic it will be using the same solvent. Aromatic carbon content varies between 25 per cent and 50 per cent for high solvency process oils.

Sulphur tends to be held in the heterocyclic structures and therefore in this portion of the oil. A complete analysis by liquid chromatography shows interesting variations in the proportions of different molecular types between fractions extracted from different crudes.

Typical hydrocarbon structures for two naphthenic oil extracts are shown in Table I. Separation was achieved by passing a small quantity of oil through

TABLE I
Hydrocarbon Analyses of Naphthenic Oil Extracts

Hydrocarbon analysis % wt	High-sulphur crude	Low-sulphur crude
Saturates	8	18
Mono-aromatics	22	35
Di-aromatics	38	29
Poly-aromatics	19	14
O_2 and N_2 compounds	9	4
Aliphatic sulphides	3	—
Poly-functional sulphides	1	—

two chromatography columns, each filled with alumina, but differing in their degree of polarity. Further separation was accomplished by elution with a number of solvents of increasing polarity (Synder).

This distribution can have a bearing upon the relative solvency, the effective uses and any potential hazard to health. Most health hazard is associated with the poly-aromatic group, and recommendations for safe use of aromatic petroleum oils have been given by the Institute of Petroleum Advisory Committee on Health.

Low Solvency Process Oils

Low solvency process oils contain a high proportion of saturated hydrocarbons and aromatic components containing much smaller amounts of the highly con-

densed aromatic structures. They are pale coloured, with good colour stability and low odour. Compared with the high solvency portion from the same distillate they have a lower ambient temperature viscosity. Their viscosities vary from 8 to 500 cSt at 40 °C, compared with 15 to 2000 cSt for the equivalent high solvency portions.

The sulphur content of these is normally less than 1 per cent, a quarter of that found in the other type, and the aromatic carbon content is typically between 1 per cent and 15 per cent.

Uses

High solvency process oils are used to chemically modify and/or extend drying oils, such as linseed and tung oil, polymers, bitumen, and various natural and synthetic resins. The physical properties of the product are changed and the oxidation/drying characteristics are influenced. They are used in the manufacture of printing inks, water proofing, compositions, foundry core oils, rubber goods, and dark PVC products.

Low solvency oils have only a slight chemical effect, and are used as carriers, dispersants, diluents, softeners, and viscosity modifiers.

Applications for the two types overlap, since a pale oil with a limited degree of solvency may be required. Such needs are met by colour improvement of high solvency types or controlled solvent extraction to enhance the solvency of a normally low solvency type. Thus a typical low solvency oil of 7 per cent aromatic carbon concentration may be produced with 10 per cent to meet certain applications. By these modifications process oils suitable for use in light coloured rubber goods and emulsions of various kinds are available.

METALLURGICAL OILS

The section deals with the application of oils and related fluids during the heat-treatment of metal alloys by processes of controlled cooling from elevated temperatures. The fluids provide environments during this quenching operation which enable new internal structures to develop within the component.

Heat-treatment of metals includes any thermal processes which change the mechanical properties. Prominent amongst such processes are those which entail heating the part to a specific high temperature followed by cooling in a prescribed manner. Until the turn of the century only 'plain carbon' steels were produced in large quantities and heat-treatment was confined mainly to treatments which improved cutting properties and wear resistance. Metallurgical progress has resulted in considerable cost and strength benefits arising from heat-treatment of cheaper alloys. The requisite strength can now be achieved from lower weight components.

The hardness of a metal is mainly dependent on the formation within it of certain physical structures; in steel the hardness is determined by martensite, pearlite, or bainite produced during the quenching process. These structures are produced when steels of different compositions are rapidly cooled. This is usually effected by immersing the hot metal into a relatively cool liquid.

Quenching Fluids

In the early days of heat treatment the range of quenching fluids was water, vegetable oils (e.g. rape seed), and marine oils (e.g. whale). Plain carbon steels could be quenched into water without cracking, but alloy steels required the slower cooling rates achieved by natural oils. Natural oils readily oxidized and have now been superseded by the more stable and less expensive mineral oils. The gap between the rapid rate of cooling of water on the one hand and mineral oils on the other has now been bridged by accelerated mineral oils and water-soluble polymer quenchants.

The metallurgist has a choice of a wide range of quenching media having extremely versatile characteristics. Considerable work has been done to produce laboratory tests to identify these characteristics and monitor their changes in use. Changes which occur in service are to water content, flash point, acidity, heptane insolubles, and additive levels. Simulated tests which reproduce the thermal shocks to which quenching media are subjected endeavour to accelerate ageing. The way in which these degradation products influence cooling characteristics can be studied in laboratory quenching tests.

Laboratory Quenching Tests

One of the earliest tests for determining the cooling rate of a quenching oil was the Nickel Ball Quenchometer which made use of the fact that nickel, like many steels, can be magnetized at room temperature, but is non-magnetic above its Curie point of 354°C. After pre-heating to 850°C and quenching, the time taken for it to become magnetic is a measure of the efficiency of the quenching medium to extract heat. This method only determines a time interval and precludes detailed study of the various quenching stages. For many applications it is essential to plot cooling rate curves and relate these to phase changes occurring during the hardening process.

The most recent items of laboratory apparatus for the study of quenching oil characteristics are developments of the Silver Ball Quenchometer. In its original form a thermocouple inserted in a silver ball, was connected to a high-speed recorder to plot the rate of cooling of the ball on immersion into the quenching medium. The CETIM apparatus, developed in France, uses a cylindrical silver test bar, whilst the Wolfson apparatus, developed in the United Kingdom, uses a much cheaper Inconel alloy test bar. Both of these tests use two different recorders; the first records the temperature of the centre of the test piece with time, and the other the same temperature versus the cooling velocity.

Many variables including surface finish, size of specimen, ratio of volume of metal to quenching medium, and thermal conductivity influence the times recorded. Only when all these are precisely defined and a standard quenching oil is available for checking apparatus parameters, as in the Wolfson method, can inter-laboratory correlation be achieved. For comparative work within the same laboratory these types of tests provide valuable data which relate to distillation range of the oil, additive depletion and contamination.

Typical cooling rate graphs (i.e. temperature against time) and cooling velocity graphs (i.e. temperature against rate of change of temperature) are

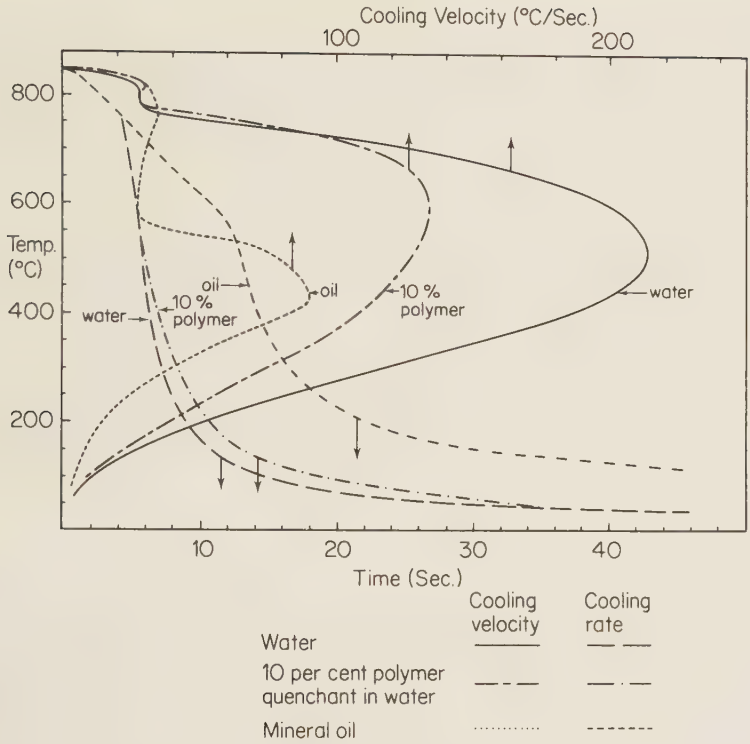

FIG. 1. Quenching characteristics by immersing Wolfson Inconel probe at 850°C into quenchant bath at 40°C.

shown for water, a mineral oil, and 10 per cent polymer quenchant in water using the Wolfson method with an Inconel probe (Fig. 1).

The Quenching Process

Three distinct stages of cooling are observed when a piece of metal is quenched from a temperature of 800–850°C into a liquid medium at a temperature of 20–200°C. The stages are known as:

(a) *Vapour blanket.* During this stage the component is enveloped in a layer of vaporized liquid and the thermal exchange is poor.

(b) *Vapour transport.* This stage follows as the vapour envelope breaks down. It is the period of most rapid cooling, and violent boiling of the quenching medium occurs at the metal surface. Heat is removed by the production of vapour bubbles, and the size to which they grow before collapsing depends on the surface tension of the medium.

(c) *Liquid cooling.* This stage starts when the component temperature has fallen below the boiling temperature of the fluid. The cooling velocity depends on the viscosity of the fluid, the temperature of the fluid relative to components, and the degree of agitation.

Quenching Oils

To obtain the maximum quench rate from an oil would require a high-boiling fraction, to minimize the vapour blanket inhibition stage, yet a low-viscosity product to enhance the vapour transport and convection stages. These features are incompatible and a compromise consistent with the requirements of the phase changes within the alloys being quenched is required. A range of quenching oils are available to meet these demands.

Low-viscosity products have low flash points and greater fire risks. More viscous and safer oils can be used by raising the bath temperature to reduce their viscosity, but there is a limit to the advantage gained. If it is too high the rate of heat transfer is reduced as the temperature difference between it and the component diminishes.

Accelerated quenching oils are formulated to increase the rate of cooling over and above these physical factors, and enable low-temperature baths to be used. Paraffinic spindle oils with petroleum sulphonates as accelerators and other surfactants to decrease interfacial tension form the basis of quenching oils.

Flash point and fire point

It is essential when a hot steel component is quenched into an inflammable fluid that the flash point and fire point of the fluid be relatively high to minimize any potential fire hazard. The flash point and fire point of a quenching oil are governed by the type of base oil used in the formulation. A close-cut fraction has a higher flash point for a specific viscosity than has a wide fraction or a blend of two components, and is preferred for this application. Since paraffinic oils, of a given viscosity, have higher flash points than those of naphthenic oils, a close-cut paraffinic fraction forms the basis of most quenching oils.

Volatility

It is desirable that the quenching oil should last as long as possible, and that there should not be unnecessary topping up of the quenching bath. Every time a component is quenched and drawn out of the oil a small amount of oil will adhere to it. This, of necessity, means a reduction in the volume of the quenching oil in use and, in large engineering shops, this reduction may attain considerable proportions. If also the oil volatilizes, the rate of depletion will increase, and unpleasant working conditions may be created. The volatility of an oil is governed by the type of base oil chosen; the higher the flash point, the lower the volatility.

Oxidation resistance

Mineral oils oxidize more readily the higher the temperature of the oil. To withstand the immersion of a steel component at very high temperature a quenching oil must be extremely resistant to oxidation. An oil of poor oxidation resistance would readily carbonize and form acidic sludges. This leads to blockage of the cooling coils in the quenching oil tank which are used to

maintain the quenching medium at a specific temperature. An oxidized oil will deposit carbon on the components being heat treated, leading to dirty work. In formulating a quenching oil, a mineral oil is chosen with the highest possible resistance to oxidation, and if an oxidation inhibitor is used it must be of low volatility.

Cleanliness of workpiece

A decade ago, it was general practice to clean, perhaps sand blast, and then machine components which had been quenched, to obtain an acceptable surface finish and appearance. The use of modern quenching oils and quenching equipment which produces an inert atmosphere, during the heating process, of either endothermic or exothermic gas, means that components are as clean and bright after quenching as prior to heat treatment, providing other good housekeeping practices apply.

Tempering Oils

Even after quenching, although the component may be neither cracked nor distorted, internal stresses are set up in it as a result of the thermal cycle that it has undergone. Thus, it is common practice after quenching to alleviate these stresses by tempering. The quenched component is re-heated to a temperature appropriate to the particular steel or alloy, and is then subjected to a second quench to reduce the temperature as quickly as possible to prevent temper brittleness and oxidation at the surface.

It was formerly common practice to heat the component in either a tempering oil or a salt bath—the particular medium chosen depending on the tempering temperature for the particular steel or alloy. For the majority of steels the normal temperature range lies between 200 and 650 °C and tempering oils would be chosen for the lower end of this range (200–300 °C). Thus, oils for use as tempering oils were chosen with the highest possible flash point, approximately 330–340 °C, and it was quite feasible to use an oil up to 300 °C or slightly higher, but these conditions were so severe that the service life of tempering oils was short, and the oil was subject to sludging and thickening far more than is the case with any quenching oil. Thus the use of tempering oils has declined, mainly because of the extremely dirty condition in which components emerged from tempering baths.

Tempering of components is now conducted in an air furnace. At the lower end of the range, an inert atmosphere may not be deemed necessary, but at the higher temperatures of 600–650 °C it is generally necessary to have an inert atmosphere. After tempering, the component is cooled as quickly as possible to prevent temper brittleness. The medium generally chosen is a soluble oil emulsion which prevents corrosion of the component whilst in the emulsion, and also affords a degree of protection afterwards.

Polymer Quenchants

Solutions of synthetic water-soluble polymers in water have been introduced as alternatives to oil quenchants.

The quench rate characteristics of water and an oil, using the Wolfson method, are shown in Fig. 1 compared with a polymer quenchant solution. By varying the concentration of the polymer and the bath temperature it is possible to cover a range of quenching speeds, and these can be adjusted to produce a desirable hardness in the alloy being treated.

Polymer quenchants are less versatile than mineral oils. They must be carefully controlled in use to ensure that the level of corrosion inhibitor is adequate and the polymer concentration is correct. A change of a few per cent can radically change the quenching properties.

They work by virtue of the inverse solubility of the polymer in water. As the temperature rises the polymer comes out of solution and the film on the component controls the rapid heat loss normally associated with water. The inverse solubility can give rise to problems in quench furnaces if the bulk temperature of the quenchant rises. Very careful consideration has to be given to circulation of the quenching fluid when using this type of medium to prevent local overheating with resultant separation.

HYDRAULIC FLUIDS

Hydraulic transmission of power was first commercially exploited in a patent for a hydraulic press taken out in 1795. At that time, water was the only suitable fluid available, since Drake had not yet discovered oil. The use of the principle extended rapidly, but for a century the size of the systems precluded the use of any other hydraulic fluid.

Today applications of fluid power have expanded into most industries. No longer is it limited to hydraulic presses and machine tools which were for many years the major areas of activity. By combining the flexibility of electrically operated valves with the expertise of the precision engineer, extremely complex mechanisms are now in service. Their working lives would, however, be intolerably short if the hydraulic fluids had not been continuously reformulated to cope with the increasingly severe conditions.

The most common hydraulic fluids are based on low-viscosity mineral oils, but the increased cost of oil, a tenfold increase in the last ten years, has caused manufacturers and users to devote more attention to aqueous-base products. Fire-resistant fluids, other than aqueous-based ones, have also increased in popularity in recent years in an endeavour to satisfy the requirements of the Health and Safety at Work Act 1974. If a system filled with hydraulic fluids and working at high pressure, up to 140 bars, fractures or leaks the fluid released atomizes forming a fine mist which may ignite on a hot surface. For applications near boilers or on hot die presses fire-resistant fluids are preferred. On large systems working at low pressures where economics rather than performance are important, aqueous-base fluids predominate.

Whichever type of hydraulic fluid is used it must transmit efficiently both pressure and power, and at the same time be relatively incompressible. It must flow freely, lubricate the pump satisfactorily and yet not escape too readily through clearances or past seals. It should be inert to metal used in construction, and not affect adversely seals and parts used throughout the hydraulic equipment.

Types and Definitions of Hydraulic Fluids

A wide range of hydraulic fluids having totally different compositions led to products being used on applications for which they were unsuitable. To regularize the description of fluids so that manufacturers and users could relate more closely, the following description of hydraulic fluid types has been adopted internationally.

HM	Mineral oils possessing particular anti-oxidation, anti-corrosion, and anti-wear properties.
HV	Fluids of form HM possessing improved viscosity/temperature properties.
HFA	Fire-resistant fluids of the oil-in-water emulsion type.
HFB	Fire-resistant fluids of the water-in-oil emulsion type.
HFC	Fire-resistant fluids of the water-polymer solution type.
HFD	Fire-resistant fluids of the synthetic type containing no water.

Oil-Base Hydraulic Fluids: Types HM and HV

Mineral lubricating oils are near ideal hydraulic fluids; not only do they act efficiently as hydraulic media, but they also minimize friction and wear, prevent corrosion, and provide a seal between moving parts. Moreover, they are universally available. Their most important characteristics are as follows:

Viscosity

British Standard 4231:1967 was introduced to assist users of mineral oils in the selection of oils of suitable viscosity for their particular purpose. Other systems for classifying industrial liquid lubricants were simultaneously under study in America by the American Society for Testing and Materials (ASTM) in collaboration with the American Society of Lubrication Engineers (ASLE), and by the Deutscher Normenausschuss (DNA). As a result ISO 3448–1975 was prepared to meet international needs. A significant change introduced in this standard is the replacement of the previous conventional reference temperature of 100°F (37.8°C) by the new one of 40°C. Table II is abstracted from ISO 3448–1975 (E).

The standard lists a series of Grades from 2 to 1500, covering products from kerosine to very high viscosity gear oils. Hydraulic oils are usually encompassed by Grades 7 to 150, from which an oil of suitable viscosity can be selected that will flow freely, and provide adequate lubrication and sealing in the system for which it is intended.

Viscosity/temperature characteristics

All hydraulic oils decrease in viscosity with increase in temperature. However, the rate of change of viscosity and change of temperature is greater with oils of a low viscosity index (VI) than with those of high viscosity index. A good quality base oil for a hydraulic oil will have a VI as high as 100, but some oils of very low pour point have a much lower VI. Whilst viscosity index is a convenient expression to indicate that the viscosity of some oils varies more than that of others when the temperature is varied, it is not easy to determine from it the

TABLE II

ISO Viscosity Classification with Corresponding Kinematic Viscosities at Various Temperatures for Differing Viscosity Indices

ISO viscosity grade	Kinematic viscosity range cSt at 40°C	Approximate kinematic viscosity at other temperatures for different values of viscosity index								
		Viscosity index = 0			Viscosity index = 50			Viscosity index = 95		
		cSt at 20°C	cSt at 37.8°C	cSt at 50°C	cSt at 20°C	cSt at 37.8°C	cSt at 50°C	cSt at 20°C	cSt at 37.8°C	cSt at 50°C
ISO VG 2	1.98–2.42	(2.82–3.67)	(2.05–2.52)	(1.69–2.03)	(2.87–3.69)	(2.05–2.52)	(1.69–2.03)	(2.92–3.71)	(2.06–2.52)	(1.69–2.03)
ISO VG 3	2.88–3.52	(4.60–5.99)	(3.02–3.71)	(2.37–2.83)	(4.59–5.92)	(3.02–3.70)	(2.38–2.84)	(4.58–5.83)	(3.01–3.69)	(2.39–2.86)
ISO VG 5	4.14–5.06	(7.39–9.60)	(4.38–5.38)	(3.27–3.91)	(7.25–9.35)	(4.37–5.37)	(3.29–3.95)	(7.09–9.03)	(4.36–5.35)	(3.32–3.99)
ISO VG 7	6.12–7.48	(12.3–16.0)	(6.55–8.05)	(4.63–5.52)	(11.9–15.3)	(6.52–8.01)	(4.68–5.61)	(11.4–14.4)	(6.50–7.98)	(4.76–5.72)
ISO VG 10	9.00–11.0	20.2–25.9	9.73–12.0	6.53–7.83	19.1–24.5	9.68–11.9	6.65–7.99	18.1–23.1	9.64–11.8	6.78–8.14
ISO VG 15	13.5–16.5	33.5–43.0	14.7–18.1	9.43–11.3	31.6–40.6	14.7–18.0	9.62–11.5	29.8–38.3	14.6–17.9	9.80–11.8
ISO VG 22	19.8–24.2	54.2–69.8	21.8–26.8	13.3–16.0	51.0–65.8	21.7–26.6	13.6–16.3	48.0–61.7	21.6–26.5	13.9–16.6
ISO VG 32	28.8–35.2	87.7–115	32.0–39.4	18.6–22.2	82.6–108	31.9–39.2	19.0–22.6	76.9–98.7	31.7–38.9	19.4–23.3
ISO VG 46	41.4–50.6	144–189	46.6–57.4	25.5–30.3	133–172	46.3–56.9	26.1–31.3	120–153	45.9–56.3	27.0–32.5
ISO VG 68	61.2–74.8	242–315	69.8–85.8	35.9–42.8	219–283	69.2–85.0	37.1–44.4	193–244	68.4–83.9	38.7–46.6
ISO VG 100	90.0–110	402–520	104–127	50.4–60.3	356–454	103–126	52.4–63.0	303–383	101–124	55.3–66.6
ISO VG 150	135–165	672–862	157–194	72.5–86.9	583–743	155–191	75.9–91.2	486–614	153–188	80.6–97.1
ISO VG 220	198–242	1 080–1 390	233–286	102–123	927–1 180	230–282	108–129	761–964	226–277	115–138
ISO VG 320	288–352	1 720–2 210	341–419	144–172	1 460–1 870	337–414	151–182	1 180–1 500	331–406	163–196
ISO VG 460	414–506	2 700–3 480	495–608	199–239	2 290–2 930	488–599	210–252	1 810–2 300	478–587	228–274
ISO VG 680	612–748	4 420–5 680	739–908	283–339	3 700–4 740	728–894	300–360	2 880–3 650	712–874	326–393
ISO VG 1 000	900–1 100	7 170–9 230	1 100–1 350	400–479	5 960–7 640	1 080–1 330	425–509	4 550–5 780	1 050–1 290	466–560
ISO VG 1 500	1 350–1 650	11 900–15 400	1 660–2 040	575–688	9 850–12 600	1 640–2 010	613–734	7 390–9 400	1 590–1 960	676–812

Note: Values in parentheses have been derived by extrapolation and are approximate.

viscosity of a fluid at its working temperature. However, viscosity/temperature graphs are available for design calculations. In some instances, where hydraulic systems are subjected to extremes of temperature, the viscosity characteristics of straight oils are unsuitable, the oils being too viscous at the low temperature and too fluid at the high temperature. It is possible to compensate for these changes by using VI improvers consisting of long-chain polymers, but under high rates of shear these polymers may slowly degrade and lose their effectiveness (e.g. Type HV).

Two methods for measuring the shear stability of polymer-containing oils are available. IP 294/79 covers procedures for mechanically stressing the test fluid by passing it through a circuit incorporating a diesel injector nozzle and a diesel injector fuel pump. Hydraulic oils need 250 to 500 passes through the injector to produce significant permanent viscosity losses.

IP 351/81 utilizes the FZG rig which is designed for the evaluation of the load-carrying capacity of gear lubricants (Refer IP 334/80). Test conditions capable of producing permanent viscosity losses in hydraulic fluids are specified in this method.

Although it is now possible to provide oils which do not degrade unduly under the normal conditions in a hydraulic system, it is still standard practice to formulate hydraulic oils with a mineral oil having as high a natural VI as possible, and to resort to VI improvers only for special products. If the viscosity of a hydraulic fluid decreases too quickly with rise of temperature, that is the VI is too low, there could be inadequate lubrication of the hydraulic pump at elevated temperatures and a greater risk of leakage.

Compressibility

When system pressures were low it was unnecessary to make allowance for the compressibility of the hydraulic fluid, since the volume change was insignificant. With the tendency to higher working pressures in hydraulic circuits there was a demand from designers for information on the compressibility characteristics of various types of hydraulic fluid. The compressibility of a normal hydraulic oil can be estimated from a knowledge of either its density or its viscosity at atmospheric pressure and 20°C, using the following equations:

$$\bar{K}_S = \{1.57 + 0.15 \log \eta\}\{\text{antilog } 0.0024(20 - T)\} \times 10^4 + 5.6P \text{ bar}$$
$$\bar{K}_S = \{1.78 + 7(\rho - 0.86)\}\{\text{antilog } 0.0024(20 - T)\} \times 10^4 + 5.6P \text{ bar}$$
$$\bar{K}_T = \{1.30 + 0.15 \log \eta\}\{\text{antilog } 0.0023(20 - T)\} \times 10^4 + 5.6P \text{ bar}$$
$$\bar{K}_T = \{1.51 + 7(\rho - 0.86)\}\{\text{antilog } 0.0023(20 - T)\} \times 10^4 + 5.6P \text{ bar}$$

where $\bar{K}_S$ = isentropic secant bulk modulus, at pressure P and temperature T, in bar.

$\bar{K}_T$ = isothermal secant bulk modulus, at pressure P and temperature T, in bar.

P = pressure, in bar.

T = temperature, in deg C.

η = kinematic viscosity at 20°C and atmospheric pressure, in centistokes.

ρ = density at 20°C and atmospheric pressure, in kilogrammes/litre (or specific gravity).

The corresponding equations with pressures and bulk moduli expressed in lb/in^2 and all other quantities in the same units as before are as follows:

$$\bar{K}_S = \{2.28 + 0.22 \log \eta\}\{\text{antilog } 0.0024(20 - T)\} \times 10^5 + 5.6P \text{ lb/in}^2$$
$$\bar{K}_S = \{2.58 + 10(\rho - 0.86)\}\{\text{antilog } 0.0024(20 - T)\} \times 10^5 + 5.6P \text{ lb/in}^2$$
$$\bar{K}_T = \{1.89 + 0.22 \log \eta\}\{\text{antilog } 0.0023(20 - T)\} \times 10^5 + 5.6P \text{ lb/in}^2$$
$$\bar{K}_T = \{2.19 + 10(\rho - 0.86)\}\{\text{antilog } 0.0023(20 - T)\} \times 10^5 + 5.6P \text{ lb/in}^2$$

Within the range 0–800 bar and 5–100°C these equations generally lead to values accurate to within about 5 per cent for all oils of viscosity ranging from 30–1500 cSt at 20°C, except oils containing a substantial proportion of viscosity index improver. With oils of very low viscosity and viscosity-index-improved oils the density-based relationships should be used in preference to the viscosity-based equations, but with such oils the estimates are likely to be rather less accurate.

Oxidation stability

During use, a hydraulic oil is pumped through a system at high pressures. The temperature of the oil rises and, as most hydraulic equipment contains copper or cuprous alloys which act as oxidation catalysts it is essential that the hydraulic oil be resistant to oxidation. All hydraulic oils contain dissolved air, and even when this air has been used up the oil is capable of absorbing more air from the space in the header tank. It is common practice to inhibit hydraulic oils against oxidation, the most commonly used additives being hindered phenols and/or amines.

Anti-wear properties

With the increased performance expected from modern hydraulic oils, an important criterion is that they should protect the pump against wear. There are many types of hydraulic pumps marketed, such as gear, vane, or slipper, each with its own particular material of construction. Anti-wear additives are incorporated in hydraulic oils to minimize wear of the pump, phosphorus-containing additives commonly being employed.

Considerable development work led to the publication of IP 281/80–BS 2000 Part 281; 1982. This is a method for evaluating the anti-wear properties of hydraulic fluids using a vane pump test. Only extremely reliable oil-based fluids pass this test, at pressures up to 140 bar. The total weight losses of the steel ring and vane elements are normally less than 100 mg after 250 hours.

Corrosion prevention

Just as hydraulic oils absorb air from the atmosphere, the adventitious entry of water cannot be avoided. This occurs, apart from accidental contamination, during periods of non-use when the system cools and draws air from the atmosphere, saturated in most cases with water vapour, into the system. Thus, it is essential that the hydraulic oil prevents this water corroding the various parts, especially ferrous, of the hydraulic equipment. Corrosion is prevented by the addition to the hydraulic oil of an additive which adheres to the metal

components, and forms thereon a molecular layer. Esters of long-chain dibasic acids are generally used for this purpose.

Emulsification

The hydraulic oil, as well as protecting the materials of construction of the hydraulic system, must be capable of separating the contaminating water as quickly as possible from the oil. Selection of the base oil used in the formulation is the main factor governing demulsibility. The adventitious entry of a surface-active material, as may occur on a machine tool, or the accidental contamination of the hydraulic oil by a detergent-type oil (motor oil, etc.) will reduce the demulsibility of the fluid. Hence, particular care is needed to prevent contamination of the hydraulic oil during transfer.

Anti-foam properties

Mineral oils are relatively incompressible. However, all mineral oils dissolve a certain amount of air, the amount increasing with pressure. When pressure is reduced in a hydraulic system, for example at the reservoir, the capacity to dissolve air is reduced, and thus millions of small air bubbles are released. If the hydraulic oil does not have good defoaming properties the air will be trapped and will circulate in the oil throughout the system. Whilst the oil is relatively incompressible, the introduction of a small number of air bubbles increases the compressibility and leads to spongy hydraulics. Silicone anti-foam agents are used to confer superior anti-foam properties; parts per million are all that is required, and over-use leads to foam stabilization.

Seal compatibility

All mineral oils affect to some degree virtually all the elastomers available for use as seals in hydraulic equipment. Therefore, it is essential that the hydraulic oil be formulated to have minimum effect on seals used in hydraulic equipment. Some systems rely on a controlled maximum swelling of the sealing elastomer to prevent leakage. This is most easily accomplished by the choice of high VI paraffinic-base oils. The effect of a mineral oil on an elastomer can be predicted with a certain degree of accuracy by the determination of the aniline point—oils of high aniline point having least effect on the elastomer. Any additives incorporated into a hydraulic oil are carefully screened to ensure that they have minimum effect on elastomeric seals.

The Association of Hydraulic Equipment Manufacturers proposed a 'Seal Compatibility Index' for mineral hydraulic oils which forecast the rubber swelling characteristics of the oil by tests on a standard rubber. The test piece is a square section ring of medium low nitrile rubber; standard test rings are available. The ring diameter is measured with a taper plug gauge and noted, after which the ring is immersed for 24 h in the oil under test held at 100°C. After cooling, the diameter is measured again and the percentage diameter change (usually the percentage increase in diameter due to swelling) is calculated. The Seal Compatibility Index can be ascertained from the Table provided. It was adopted as a standard by the Institute of Petroleum in 1972 and reapproved in 1978 (IP 278/72 (78)).

Particulate contamination

The performance of hydraulic equipment can be seriously impaired by particles entrained in the fluid which may cause valves to malfunction. This applies particularly to aerospace hydraulic fluids where life is often at stake. The sampling of products to ensure they are representative and the techniques for sizing particulates are covered in IP methods 275/71, 320/75 (82), and 327/81. The first refers to microscopic examination, whilst the last covers the use of an automatic particle counter based on the light interruption principle.

High Water-Base Fluids (HWBF) : Type HFA

Oil-in-water emulsions have been used satisfactorily for many years in large systems operating at low pressure. The benefits of lower cost, better heat transfer, reduced hazard to the environment, and good fire resistance are substantial benefits in their favour. When the cost of oil was relatively low there was no incentive to widen their scope to high-pressure systems with potential lubrication problems. The cost difference between an emulsion of 5 per cent base in 95 per cent water and mineral oil fluids of types HM and HV expanded rapidly and provided the necessary impetus to evaluate them in more onerous work. A base concentrate is supplied and the mixing of the functional fluid is undertaken on site.

Limiting features for these fluids are system temperatures between 4° and 55°C, and pressures less than 60 bar. Their viscosity cannot be controlled; it is always the viscosity of water, approximately 1 cSt. This means it is often difficult to provide an adequate film of fluid to prevent pump or component wear. Anti-wear additives are included, but problems are experienced with vane and gear pumps. Most successful applications continue to be with piston pumps.

Corrosion prevention is considerably more difficult with this type of fluid than with mineral oils, and has resulted in a method being developed which is applicable to fire-resistant fluids containing water (IP 329/79). An assembly of various metals, some in electrical contact and others insulated, is partially immersed in the test fluid for 330 h at 50°C. The appearance and weight loss of the test pieces indicate the metals likely to cause problems in service. The alkaline nature of HWBFs means they are not compatible with zinc, magnesium, lead, cadmium, and un-anodized aluminium.

Seal compatibility is less of a problem with oil-in-water emulsions, but seal wear results in excessive leakage, because their viscosity is so low. Internal leakage results in an inefficient system; consequently frequent maintenance is required.

Water-in-oil Emulsions: Type HFB

Water-in-oil emulsions are chosen specifically for their fire resistance, which implies the fluid must resist ignition, be reluctant to propagate flame, and have the ability to self-extinguish when a source of ignition is removed. Numerous tests have been developed to determine fire-resistance characteristics, but tests differ between countries and even industries within countries.

They consist of water droplets up to 2 microns in diameter uniformly

dispersed throughout the continuous oil phase. In order to pass the fire-resistance tests a water content of from 40 to 45 per cent is used. Most of these products are manufactured to the ISO VG 68 and 100 viscosity standards of conventional type HV and HM mineral oil fluids (Table I). To ensure a constant viscosity, stable emulsions are prepared using sophisticated high-shear homogenizers. Emulsion stability testing is important to ensure that droplet coalescence with subsequent water separation does not occur. These products, unlike oil-in-water emulsions, are only supplied ready for use.

Type HFB fluids have been used satisfactorily in axial piston pumps and gear pumps up to 20 MPa, but vane pumps are restricted to operations at about one third of this pressure. They give good service between 0 and 70 °C, but higher temperatures are excluded as the vapour pressure rises, and the viscosity falls. High standards of filtration (5–15 μm) are required with full-flow filters on the pressure side capable of accepting twice the pump output. Epoxy resin-impregnated paper elements have proved satisfactory, and maintenance by replacement is recommended. On the inlet side of the pump a strainer element having a nominal pore size larger than 70 μm, supplemented by a magnetic particle arrestor, is generallly used.

Water Glycol Fluids: Type HFC

They contain in general from 40 to 45 per cent water in various combinations of glycols and polyesters depending on the viscosity required. Various additives are incorporated to modify or improve certain characteristics. They comply with requirements for fire resistance in the mining industry, but become less fire resistant as increasing numbers of additives are incorporated to meet wear tests.

In general, water polyglycol fluids have longer de-aeration times than mineral oils. This should be taken into account in the design of tanks by providing for a longer residence time. Care should be taken that the fluid is returned to the tank, without agitation, below the air–liquid interface. A maximum operating temperature of 70 °C is possible but the normal operating temperature range is −20 to 50 °C, thereby limiting evaporation.

It is important to measure the water content regularly and to adjust if necessary by adding de-ionized water. They are single-phase mixtures, and adjustments of the water content during service are easily done. Because they have peptization characteristics solids remain in suspension; hence it is necessary to provide large-capacity filters to avoid rapid wear. Woven metal or nylon filters and special papers are suitable, but absorbing filters which could remove additives should not be used.

This type of fluid tends to be used when non-flammable properties are required and oil-in-water emulsions type HFA give insufficient lubricating properties.

Synthetic Hydraulic Fluids: Type HFD

Synthetic hydrocarbons

These products are based on oligomerization of α-olefins and are the result of a requirement for a less flammable direct replacement for mineral oil

hydraulic fluids, types HM and HV. They are compatible with all system materials and are completely miscible with mineral oils. Their main advantages over mineral oils are high flash points $>200^{\circ}$C, fire points $>250^{\circ}$C, and auto-ignition temperatures $>340^{\circ}$C. They have a naturally high viscosity index and require no VI improvers; consequently they are shear stable. They have been widely adopted for aircraft hydraulic systems, since they may be used from approximately -50°C to 200°C.

Phosphate esters

Phosphate esters are manufactured from either coal tar or petrochemical phenols (to produce the aryl esters), or alcohols (to produce the alkyl esters). For a given type the finished product is usually a mixture of esters, because the starting material is normally an impure commercial grade.

They were the first class of synthetic based hydraulic fluids to gain wide acceptance in the aerospace industry, and are used extensively in control systems of turbine and boiler hydraulic equipment. Careful selection of the system components is required, since they are somewhat more aggressive than mineral oils. Servo-valve erosion characteristics, thermal stability, and tolerance to chemical contamination have all been improved during their development over the past ten years.

Silicate esters

Silicate esters are similar to phosphate esters, except that the phosphorus atom of the latter is replaced by a silicon atom. They have operational capability down to -54°C. Their major deficiency is poor hydrolytic stability.

Glycol ether esters

This range of synthetic hydraulic fluids is predominant in brake fluids. The inherent moisture absorption in brake fluids due to the hygroscopic nature of mixed glycol ether based fluids has largely been overcome by the use of mixed glycol ether esters, as a major constituent of the brake fluids formulation. Moisture absorption has the effect of decreasing the boiling point of the fluid, increasing its low-temperature viscosity and promoting greater corrosion.

TEXTILE OILS

The upsurge in the production of synthetic fibres has involved a whole new range of problems to be resolved by textile oils. The term textile oil is usually applied to the specific products used in the conversion of raw materials to finished fabrics in a complex mechanical process. The section excludes the products required to lubricate the machinery.

Most natural textile fibres, whether of animal or vegetable origin, are relatively short in length and, therefore, have to be worked into such a physical arrangement as to produce a continuous yarn of reasonable strength. Synthetic fibres, on the other hand, are produced as clean continuous filaments, and

processes associated with orientation of natural fibres and removal of foreign matter (e.g. seeds, stalks, dust, generally known collectively as trash) are eliminated. Since the purpose of a lubricant is different when natural and synthetic fibres are processed separately or together, the characteristics of textile oils must be tailored for the operation. The requirements of the spinning and finishing trades are different, but the residual lubricants in the yarn from a number of spinners must be compatible with the sophisticated finishing processes.

Characteristics Required for Natural Fibre Processing

Baled cotton as it arrives at the mill contains varying amounts of foreign matter and about 60 per cent is removed in the blowing room after which it is carded to open it into single fibres to produce a sliver. The sliver is then combed and paralleled, and the rovings are twisted and spun. These operations are liable to produce a lot of airborne dust and fluff, particularly in waste mills, upholstery and mattress-filling industries, and preconditioning by application of textile oil emulsions is widely practised to suppress it. Once applied the oil must also lubricate and protect the fibres, and reduce static electricity between them and between the fibres and the contacting machining elements.

Traditionally lubricants are applied to wool at levels in the range from 5 to 10 per cent (by weight of fibre). In order that they may be effective they must be applied evenly over the entire blend. This is particularly difficult with low-level applications, and emulsions of oil and water can be applied more easily in proportionately larger weights. The added water is an important contributor to the final yarn condition. Specialized applicators are required to ensure even distribution. This applies particularly in the production of knitwear when the wool is returned to the spinner after dyeing, and the lubricant must carry it through the subsequent processes of carding, spinning, and knitting.

The characteristics of the lubricant to make it satisfactory for spinning are that it should be stable to light and oxidation to avoid leaving deposits after prolonged storage which are difficult to remove. It must reduce fibre friction to a level such that unacceptable fibre-breakage does not occur. Excess fibre-breakage would give a lower mean fibre length, a weaker yarn, and lower yield. Fibre–fibre cohesion must not be hindered, otherwise poor sliver separation and condensing will result, giving eventually poor fibre yields. Finally, it must be readily removable in subsequent scouring with the machinery available.

The lubricants used can be divided into four types: oleines, semi-neutral oils, mineral oils, and synthetic products. Most of these contain a proportion of highly refined mineral oil which is solvent-extracted, with stability characteristics and electrical properties similar to transformer oils. Indeed, in some applications such as surgical dressing, impregnation with technical white or medicinal oil is preferable.

The most widely employed oleine is a blend of 70 per cent commercial oleic acid and 30 per cent mineral oil. Its main advantage is that during scouring it is converted to soap by the addition of soda ash, and thus has a high scouring and milling power. The oleine group of lubricants, whilst the oldest, is still amongst the most effective. Semi-neutral oils are essentially oleic acid and mineral oil with added glycerides, and non-ionic emulsifiers to make the oils emulsifiable.

They provide good fibre lubricity and control during spinning, and improve fibre–metal lubricity.

Mineral oils are those types consisting only of a blend of oil and non-ionic emulsifiers. They tend to be cheaper than the former types, lower in viscosity, and can be scoured under neutral or mildly alkaline conditions. Alkaline scouring formulations suitable for oleines are unsuitable for this type.

Synthetic products are more complex than the others, and are intended to give greater flexibility of processing. They provide a composition which gives easier removal, and often contain synthetic surfactants, i.e. ethylene oxide–propylene oxide copolymers. In general they have limited applicability.

Textile oils which are applied neat are formulated with additives that impart self-scourable or readily scourable properties. The main groups of additives are detergents and emulsifiers, for example, anionic sodium petroleum sulphonates and/or blends of non-ionic surfactants. Oxidation inhibitors may be required and anti-static agents are usually present.

Characteristics Required for Synthetic Fibre Processes

Where the fibre is produced from a spinnerette or from fibrillated tape some lubrication is necessary in the process of converting it into yarn. Mineral oil based lubricants are generally applied neat, but synthetic lubricants are often applied as an emulsion. The lubricants are applied in carefully controlled amounts after any draw-texturing process and before winding. Over-lubrication should be avoided to prevent uneven distribution in package, and the type of lubricant must be considered in terms of the end-user of the yarn, to ensure that it is compatible with any further processing.

A finished lubricant must be much more than an oil; it must be a balance of lubricant, emulsifier, and anti-static agent. The chemical interaction of these may interfere with their prime functions if they are not compatible. Static is a big problem with man-made fibres, and without protection problems of distortion, metal adhesion, and entangled yarns inevitably result.

Emulsifying Scourability Properties

The concept of hydrophile–lipophile balance is useful but, since it is qualitative, it has restricted value in textile formulations, and supplements, rather than replaces, practical assessment of emulsion stability. It is useful to test for emulsion stability in soft and hard (20°C) waters by self-emulsifiable (SE) and conversion (C) techniques. In the former method 10 ml textile oil is added to 90 ml water in a graduated cylinder and the mixture is vigorously shaken. By the alternative (C) technique water is added in 2-ml increments to 20 ml of textile oil in a 100-ml graduated cylinder with vigorous shaking until the inversion stage is reached, as indicated by frothing and reduction of the emulsion viscosity. After inversion water is added rapidly to 100 ml. The emulsion is then allowed to stand at room temperature and after 24 h there should be no evidence of instability by oil or water separation, and no more than 2 ml creaming at the emulsion surface.

Various systems are used to spray emulsions in carefully controlled

quantities. They normally comprise a concentrate storage tank, a mixing unit, an emulsion storage tank with stirrer, and spray unit.

Whilst in many instances textile oils are allowed to remain in the end-product, it is common practice to examine the finished fabric under ultra-violet light to detect either machinery lubricant contamination or inadequacies in the method of application. All textile oils are tested for their ability to be scoured from the yarn.

Textile oils produce a cleaner environment, reduce waste losses, and provide secondary benefits to subsequent processes.

PETROLEUM SULPHONATES

Petroleum sulphonates are produced either from distillation cuts in the refining of crude oil or from alkylated aromatic compounds. When produced from crude oil they are termed 'natural' sulphonates to distinguish them from 'synthetic' alkyl benzene compounds. Dependent on molecular or equivalent weight they are either water- or oil-soluble. Despite this sub-division the term petroleum sulphonates has usually been identified with 'natural' sulphonates which are in the main oil-soluble.

Manufacture

In the historical sense the manufacture of petroleum sulphonates has been related to the treatment of naphthenic and paraffinic lubricating oil fractions, using oleum or sulphur trioxide, to produce medicinal and technical white oils. The purpose of the treatment is to remove the aromatic compounds remaining in the mineral oil, and these are taken out as petroleum sulphonates. The reactions which occur between the feed and the reagent include oxidation, polymerization, and dehydrogenation, but the essential one is sulphonation due to the electrophilic substitution of the SO_3 group into aromatic ring systems. The sulphur atom of sulphur trioxide is highly electron-deficient, and it is this atom, therefore, which becomes bonded to a ring carbon atom, namely,

$$R{-}C_6H_5 + SO_3 \longrightarrow R{-}C_6H_4{-}SO_3H$$

It should be stressed that nowadays white oil production is tending more to the saturation of the aromatic components by severe hydrogenation, and petroleum sulphonate manufacture has to stand up in its own right, i.e. divorced from the needs of co-produced white oils. Over the last ten years consideration has been given to sulphonating lube distillates, atmospheric residues, or even crude oil itself, to meet the needs of a cheaper product in the utilization of sulphonates in the tertiary recovery of crude oil, of which more will be said later.

Over the last thirty-five years the main route to sulphonate manufacture has been to take a lube oil distillation cut, boiling above 300°C, refined to a raffinate by solvent extracting out some of the more condensed ring aromatics, and then sulphonating the raffinate, which would normally contain between 5 and 40 per cent of aromatic and a small quantity of polar compounds. The aromatics would be mainly mono—but there would be some di- and poly-aromatics. The polar compounds would consist of sulphur, nitrogen, and

oxygen components. With such a range of components their sulphonation products contain a series of sulphonic acids of complex structure and varying solubility, and it comes as no surprise that not all are soluble in the refined hydrocarbon. In most commercial units a sludge separates from the oil phase. The sludge, which is a mixture of sulphonic acids, water, resinous material, excess sulphonating agents and co-extracted mineral oil, creates an environmental disposal problem. The sulphonic acids which remain in the oil phase have been termed 'mahogany' acids, and those appearing in the sludge 'green' acids. This colour differentiation was more pertinent to the use of oleum; the advent of sulphur trioxide produced acid sludges where the colour of the entrained sulphonic acids was the same as that of those recovered from the oil phase.

The normal technique for recovering sulphonic acids from the oil phase is to neutralize them with sodium or ammonium hydroxide and to extract them with aqueous alcohol. The separated raw soap phase is further refined to remove dissolved inorganic salts, and then stripped of solvent to give an oil-soluble concentrate. Alternatively, the sulphonic acids can be extracted without neutralization when the salts of alkaline earth metals are the desired end-product. This route causes more complication in the removal of entrained inorganic acids.

Although it follows that the sulphonate yield will depend on the concentration and structure of the aromatic components of the raffinate feeds, a variety of techniques have been applied to increase the yield. These include:

(1) Pre-conditioning the feed by processes which preferentially abstract the more aromatic or polar compounds, such as dilute acid treatment, further solvent extraction, or hydrogenation—if these compounds were not removed, most would migrate to the sludge taking with them some of the 'good' sulphonic acids from the oil phase;
(2) Diluting the sulphur trioxide reagent with an inert gas or liquid, in order to moderate a highly exothermic reaction;
(3) Increasing the number of sulphonation treatments by using lower sulphur trioxide to oil ratios, and applying intermediate sulphonate extractions;
(4) Quenching the reaction very quickly after contact of oil and sulphonating agent, using water, ammonia or dilute alkali, thus preventing over-sulphonation and excessive sludge.

The alkaline earth neutral and basic sulphonates are important detergent additives in automotive and marine engine lubricating oils. In addition to direct neutralization of sulphonic acid concentrates with metal hydroxides they can be converted from the sodium or ammonium salts by double decomposition using the requisite metal salt. High basicity may be introduced either during or at the end of the reaction. The basic products, usually carbonated, can exhibit up to 400 base number. Electron micrography has shown that this basicity can be uniformly dispersed in the sulphonate medium as a colloidal suspension of particles (approximately 0.005 to 0.01μ).

The potential source of useful sulphonates in sludges has not been commercially exploited, mainly because of their variability and the difficulty in separating them from black polymeric material. When sulphur trioxide is used

as the sulphonating agent, the sludge separating from the acid oil can contain up to 70 per cent sulphonic acids.

Properties

The natural oil-soluble sulphonates are brown powders which are extremely hygroscopic, and for that reason are usually marketed at 50–60 per cent concentration in mineral oil as dark-brown, highly viscous liquids. A lighter colour is aesthetically appealing and can be achieved by bleaching, but this has not been commercially viable to the manufacturers.

The sulphonates consist primarily of salts of mono-sulphonic acids of approximate formula $C_nH_{2n-10}SO_3H$. There is a small amount of di- or poly-sulphonic acid salts present and these can be separated qualitatively in an analytical laboratory by high-pressure liquid chromatography. To determine the typical hydrocarbon structure petroleum sulphonates can be hydrolysed back to the parent lipophile by treatment with strong acid under pressure. Phosphoric acid gives better than 80 per cent conversion and is to be preferred to hydrochloric acid which only achieves 30 per cent. Using this technique it has been shown that the ideal hydrocarbon structure is better provided by very high viscosity index raffinates, whose aromatic components are mainly mono- and di-aromatics with relatively long carbon side-chains. Thus a raffinate from a paraffinic crude can be converted into oil-soluble sulphonates in 80–90 per cent yield based on aromatic content, compared to the order of 40 per cent from a raffinate from a naphthenic crude.

The study of the hydrocarbons obtained by hydrolysis also confirms the range and complexity of natural sulphonates. By distilling the hydrocarbons, it can be shown that a typical 470 equivalent weight commercial product can range in equivalent weight components from 400 to 650. Synthetic sulphonates which would be expected to have a lesser degree of complexity in their hydrocarbon structure still have a wide equivalent weight spread. This is illustrated in Table III by data obtained on commercial products of approximately 500 equivalent weight (EW) by hydrolysis, distillation, and analysis of the lipophile components.

The equivalent weights of the sulphonates were determined by hyamine titration. After hydrolysis the mean molecular weight of the lipophile components was cryoscopically determined. The assumption was made that each

TABLE III
Hydrocarbon Structure Analysis of Commercial Sulphonates

Type	Origin	EW	Calc. EW	R_A	R_N	C_P	EW spread
Natural	Texas crude	490	510	1.2	2.6	12.5	405–590
Natural	Middle East crude	530	555	1.0	1.7	20.7	430–655
Synthetic	—	510	535	1.0	—	25.3	420–690

where R_A* = number of aromatic rings/mean molecule,
R_N = number of naphthenic rings/mean molecule,
C_P = number of side chain carbon atoms/mean molecule.

* ASTM Method D3238-74 (1979). Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n–d–M Method.

mean molecule had been monosulphonated, which was considered adequate for comparison purposes. On that basis, the addition of 102 for the group SO_3Na replacing a hydrogen atom gave a calculated equivalent weight. By carbon composition analysis of the lipophile using measurements of density, refractive index, and molecular weight the R_A, R_N, and C_P values could be determined. Each lipophile was vacuum distilled into ten equal fractions. Determination of the mean molecular weight of each fraction then led to a calculated equivalent weight value, which could be converted into an equivalent weight spread.

The salts of petroleum sulphonates have been prepared from many metal ions such as copper, magnesium, and iron, but by far the most common one is sodium. It is their surfactant properties which have led to their widespread use in numerous industries. The changeover from water to oil solubility occurs at an equivalent weight of around 400. The strongest intermediate effect between oil and water solubility occurs in the equivalent weight range of 400 to 450. Sulphonates with a mean equivalent weight in this region have the best emulsifying ability on oil and water phases. This effect is achieved by the lowering of interfacial tension between the two phases and is only relative to sulphonate concentration until its critical micelle concentration is reached. Then sulphonate molecules combine together in units of 50 to 200 in micellar form. The equivalent weight spread is a useful property, since there is a balancing effect between the lower EW sulphonates solubilizing the higher EW ones which have the better surface activity.

Uses

Petroleum sulphonates are anionic but, unlike surface-active agents in this class, due to their complexity and consequent variable polar/non-polar character, they have much greater versatility in application. The lower equivalent weight oil-soluble concentrates find wide application in emulsifiable oils for oil-in-water emulsions for metal processing, textile, and leather industries. Whilst it is usual in emulsion technology to formulate with two or more surface-active agents, in preference to a single emulsifier, this restriction does not necessarily apply with petroleum sulphonates, and it is quite possible to produce emulsions from a balanced oil plus sulphonate system. However, mainly for economic reasons, sulphonates are rarely used alone but in combination with a variety of auxiliary emulsifiers, additives, linkage agents, and co-solvents for the particular requirements which may demand spontaneous emulsification, emulsion stability, spreading, and anti-corrosive properties.

The higher equivalent weight soaps tend to form oil-in-water emulsions less readily, but their emulsions, once formed, are extremely stable. They impart excellent metal-spreading characteristics and, especially as the calcium salts, form the basis of many rust-preventive compounds and water-in-oil emulsion systems.

They are used in de-watering fluids where the surface-active properties endow the product with the ability to displace water from metal surfaces and prevent rusting from occurring beneath an oil film. In dry-cleaning aids, sulphonates permit sufficient water to be taken into solvent solution to provide

the desirable 75 per cent relative humidity necessary to prevent shrinkage, greying, and pass-ups in charge systems.

The most important outlet for the higher equivalent weight petroleum sulphonates, particularly salts of the alkaline earth metals, is in additive packages for engine lubricants. Micelle formation provides a mechanism by which insoluble products may be solubilized in the oil. In addition, the highly basic types of sulphonate neutralize acid combustion products, preventing the formation of lacquers on engine parts. The usual metals used for high base sulphonate additives have been calcium and barium. There has been a trend towards the magnesium soap which produces a lower ash level.

Petroleum sulphonates have frothing properties and as such can be used in ore-flotation, and can be used to collect and therefore concentrate various non-metallic minerals or up-grade certain low-grade iron ores. Both oil-soluble and water-soluble sulphonates serve as agents for flotation, and this technique has been applied in areas outside the mining field.

Over the last ten years a considerable number of field trials have been carried out, especially in the USA, evaluating secondary and tertiary recovery techniques on crude oil recovery. Tertiary recovery involves chemical means, and the application of petroleum sulphonates has appeared in several patents. Typically the sulphonates form part of an alcohol/water mix in a micro-emulsion form which is pushed by a polymer drive fluid through the rock strata to release the crude oil. Here again the wide equivalent weight range of the sulphonates plays an important part. The high end of the range provides the best contribution to reduction of interfacial tension solubilized by the low end of the range. The middle portion is said to act as a sacrificial adsorbent on the rock interface leaving the remainder free to release the oil. Also in oil field operations sulphonates have been used in drilling muds, and oil well stimulation. If these uses were proved more viable than other techniques then the marketing of sulphonates for crude oil recovery would far outweigh any other use.

WHITE OILS

The terms 'white oil' or 'white mineral oil' are used to describe the range of highly refined oils which are produced from feedstocks boiling in the same range as lubricating oils.

There are three classes of white oils, recently defined by the UK White Oils Association as follows:

(a) Medicinal—a highly refined transparent, colourless (Saybolt +30 minimum, or WOMA 3, IP 17B 0.25 maximum) mineral oil, almost odourless and tasteless, complying with the requirements for Liquid Paraffin (light, medium, or heavy) of a relevant Pharmacopoeia.

(b) Food-grade—oil as described above, not necessarily complying with Pharmacopoeia requirements in respect of density and viscosity, although the latter should not be below 5 centistokes (mm^2/s) at 40 °C.

(c) Technical—a highly refined transparent, almost colourless (Saybolt +28 minimum, or WOMA 4, IP 17B 0.5 maximum) mineral oil having a viscosity not below 5 centistokes (mm^2/s) at 40 °C. and u.v. absorption in the range 240–280 nm not exceeding $E^{1\%}_{1cm}$ 1.5.

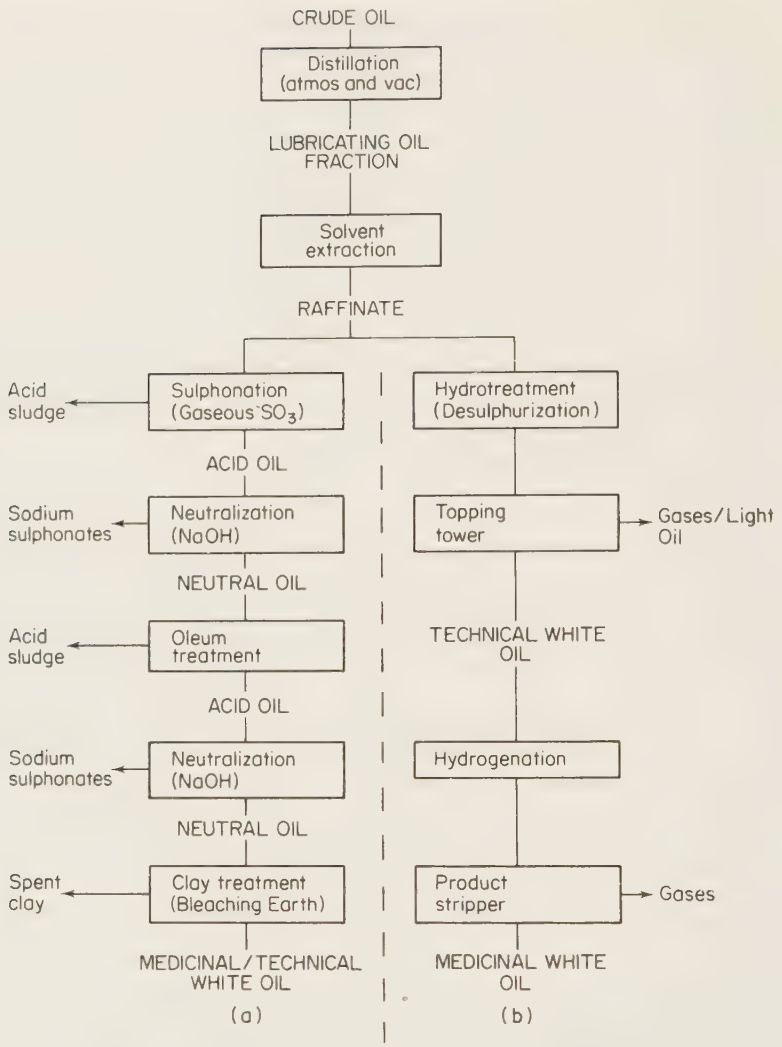

FIG. 2. Processes for manufacture of white oils (a) conventional acid process, (b) hydrogenation process.

White oils can be produced from most types of crude oil, in varying yields and degrees of difficulty, by two types of process.

The older conventional process, illustrated in Fig. 2(a), is essentially one of removal of hydrocarbons containing aromatic rings. The process involves the treatment of a suitable lubricating oil or other feedstock with acidic compounds, such as gaseous sulphur trioxide and/or oleum, in a multi-stage process. Acid sludge is formed in the reaction, and has to be removed prior to the neutralization step, which is carried out using an aqueous, alcoholic solution of sodium hydroxide. This removes the oil-soluble sulphonic acids formed in the operation, in the form of their sodium salts, which constitute a

valuable by-product. The neutralized oil is finally contacted with activated bleaching earth, which produces the required 'water-white' oil. Variation in the severity of the treatment produces medicinal or technical quality oil as required.

In the last decade the process outlined above has been superseded to a considerable extent by a variety of hydrogenation processes. These have the benefit of eliminating the production of acid sludge, the disposal of which can give rise to environmental problems. One of these processes is illustrated in Fig. 2(b), and involves a two-stage process. The first 'hydro-treatment' stage is a catalytic desulphurization process, which, after removal of hydrogen sulphide and ammonia gases, formed in the process, is followed by a topping operation which removes the low-boiling components, and produces an oil of satisfactory volatility and viscosity. The second 'hydrogenation' stage is a deep catalytic hydrogenation process, which ensures the complete saturation of all aromatic hydrocarbons present. This process can also be used to produce a full range of medicinal and technical white oils.

There is an increasing number of bodies involved in laying down specifications for medicinal and/or food-grade white oils.

In the UK those primarily concerned are the British Pharmacopoeia, covering Liquid Paraffin, the Ministry of Agriculture, Fisheries, and Food, covering food-grade oils, waxes, and white petroleum jelly, under the Mineral Hydrocarbons in Food Regulations, the Ministry of Defence, covering Light Liquid Paraffin, OM 17, and the White Oils Association. Other bodies involved include the British Plastics Federation and the Cosmetic, Toiletry, and Perfumery Association.

Other important specifications are those included in other National Pharmacopoeias such as those of USA and West Germany, the US Food and Drugs Administration, and the World Health Organization.

There has been much discussion in Europe in recent years on the establishment of a monograph covering two grades of liquid paraffin, to be included in the European Pharmacopoeia. When finally agreed this will be adopted by all of the countries participating, replacing the National Pharmacopoeias currently in force.

The more important specifications referred to above are summarized in Table IV.

There are relatively few bodies concerned with specifications for technical white oils.

In the UK the only official specification, issued almost thirty years ago, was that associated with an oil used for the lubrication of self-acting mules in the textile industry, where it was found that an inadequately refined oil could give rise to scrotal cancer in male operatives. However, the textile industry has declined to such an extent that this specification is now hardly relevant.

In the USA the Food and Drugs Administration has issued regulations covering technical white oil 'wherever mineral oil is permitted for use as a component of non-food articles' to which reference is sometimes made.

Numerous tests are applied to white oils, including the assessment of odour and taste, and tests for physical properties (density, flash point, viscosity, colour, freedom from wax at temperatures down to 0°C, etc.), but the most important are those tests designed to determine the purity of the oils involved.

TABLE IV
White Oil Specifications

	Light Liquid Paraffin				Liquid Paraffin			
	OM-17 DEF 91/36	West German Pharm.	European Pharm. (draft)	US Pharm.	British Pharm.	West German Pharm.	European Pharm. (draft)	US Pharm.
Density at 20°C	—	0.832–0.872	0.810–0.875	(0.821 0.883)	0.830 0.890	0.866 0.892	0.827–0.890	(0.848–0.908)
Flash point, PMC°C	150 min	—	—	—	—	—	—	—
Viscosity at 20°C mPa.s (cP)	—	70 max	25–80	—	—	100 min	110–230	—
Viscosity at 37.8°C mm^2/s (cSt)	—	—	—	—	64 min	—	—	—
Viscosity at 40°C mm^2/s (cSt)	12–15	(30 max)	(13.5–34)	33.5 max	(57 min)	(40 min)	(45–80)	34.5 min
Carbonizable substances	included in all							
Light absorption $E^{1\%}_{1cm}$								
at 240–280 nm	0.05 max	—	—	—	0.05 max	—	—	—
at 275 nm	—	0.016 0 max	—	—	—	0.016 0 max	—	—
at 295 nm	—	0.002 0 max	—	—	—	0.002 0 max	—	—
at 300 nm	—	0.001 5 max	—	—	—	0.001 5 max	—	—
Limit for polynuclear compounds at 260–350 nm	—	—	0.10 max	0.10 max	—	—	0.10 max	0.10 max

Note: Densities and viscosities in parentheses have been calculated from limits at other temperatures. These are approximate.

The three most important tests are as follows:

(a) Carbonizable substances—oil is shaken with an equal volume of acid of prescribed strength under specified conditions, when the colour development of the acid layer is considered an indication of purity, the purest products developing very little colour.
(b) Light absorption—measurement of u.v. absorption is a very sensitive means of detecting the presence of aromatic hydrocarbons, and limits over the ranges of 240–280 nm and 275–300 nm are specified in the British and West German Pharmacopoeias, respectively.
(c) Limit of polynuclear compounds—this test originally developed in the USA, now widely adopted, involves extraction of white oil with dimethyl sulphoxide, a solvent which has been shown to dissolve polynuclear hydrocarbons preferentially, and measurement of the u.v. absorption of the resultant extract over the range 260–350 nm.

The stability of white oils is an important feature, which can be improved by incorporating small amounts (up to 10 mg/kg) of suitable anti-oxidants such as tocopherol or butylated hydroxytoluene. Such use is permitted in the UK and USA and in some European countries. The proposed European Pharmacopoeia, referred to earlier, does not permit the use of anti-oxidants, hence when this is adopted by the British Pharmacopoeia, use of anti-oxidants in medicinal white oils will not be permitted. However, use of anti-oxidants in white oils used in food applications is likely to be continued.

White oils are used in a wide range of applications and industries, as follows:

Plastics/chemical industries—used as lubricants for ethylene and propylene compressors, as plasticizers, internal lubricants, mould release agents, catalyst vehicles, and dye dispersants.

Textile industry—used for the lubrication of textile machinery, because of their non-staining properties, and as oils for hot drawing and finishing of synthetic fibres.

Toiletry/cosmetics industry—used as a carrier or base for a wide variety of creams (beauty, cleansing, make-up, barrier, etc.), hair preparations, lipsticks, etc.

TABLE V

Proposed Specified Foods Permitted to Contain Mineral Hydrocarbon

	Food	Limit (mg/kg)
(a)	Dried fruit	2 500
(b)	Citrus fruit	1 000
(c)	Gelatine-based sugar confectionery; wine gums; jelly preparations	2 000
(d)	All other sugar and chocolate confectionery	1 000
(e)	Table jellies	2 000
(f)	Bread; fermented flour confectionery products (buns, bun loaves, chollas)	1 000
(g)	Chewing compound	150 000
(h)	Rind of pressed cheese	*
(i)	Shells of eggs	*

* Limited according to good manufacturing practice.

Food/agricultural industries—used to lubricate machinery, in canning and rolling operations, in dust suppression, foam control, preservative coatings, release agents, preparation of animal feeds, agricultural sprays, and veterinary preparations. Foods in the UK which are permitted to contain mineral hydrocarbons are listed in Table V.

Pharmaceutical industry—apart from the well known use as a laxative, used in many preparations including balms, ointments, paste bandages, etc.

INSULATING OILS

Whilst certain synthetic non-hydrocarbon materials are in service for insulating purposes, such as polychlorinated biphenyls and gaseous sulphur hexafluoride, by far the greater proportion of such service is provided by hydrocarbon oils. Polychlorinated biphenyls are now recognized as an environmental hazard. Production has eased in some countries, including the major producer, USA, and in others such as Japan, legislation has been passed banning their use. Great care should be taken when handling this material. Hydrocarbon oils are almost entirely of petroleum origin, but synthetic hydrocarbons (e.g. alkylbenzenes) are being used for certain applications such as in oil-filled cables, and interest in synthetic hydrocarbon insulating liquids is growing.

Table VI shows the characteristics of insulating oils to meet the International Specification IEC 296, and the three Classes I, II, and III refer to viscosity at ambient temperatures. The single oil in BS 148:1972 corresponds to IEC 296

TABLE VI

IEC 296 International Specification for Mineral Insulating Oil

Property	Specification		
	Class I	Class II	Class III
Kinematic viscosity, cSt at 40°C[a]	16.5 max	11.0 max	3.5 max
at −15°C	800 max		
at −30°C		1 800 max	
at −40°C			150 max
Flash point, °C	140	130 min	95 min
Pour point, °C	−30 max	−45 max	−60 max
Appearance	Clear, free from sediment and suspended matter.		
Density, kg/dm³ at 20°C	0.895 maximum		
Interfacial tension, Nm at 25°C (optional)	40×10^{-3} minimum		
Neutralization value, mg KOH/g	0.03 maximum		
Corrosive sulphur	non-corrosive		
Oxidation stability			
uninhibited oil: acid value, mg KOH/g	0.40 maximum		
sludge value, % by mass	0.10 maximum		
Breakdown voltage			
as delivered, kV	30 minimum		
after treatment, kV	50 minimum		
Dissipation factor, at 90°C and 40 to 62 Hz	0.005 maximum		
[a] Kinematic viscosity, cSt at 20°C (corresponding values)	40 max	25 max	6 max

Class I, but its maximum pour point of −30°C, adequate for Great Britain, is higher than temperatures regularly occurring in Scandinavia, Eastern Europe, Canada, and many other parts of the world. Class II oil has a maximum pour point of −45°C, and is also lower than Class I oil in viscosity and flash point. Even this oil is now considered inadequate for the low ambient temperature conditions arising in some areas, and Class III oil has been introduced into IEC 296, with a maximum pour point of −60°C. To conform with international practice, the viscosity at 20°C has been deleted, except for a reference, and one at 40°C substituted. This will also eventually be incorporated in BS 148.

Transformer Oils

The British Standard Specification

BS 148:1972 follows IEC Publication 296 (1969), except in three respects; it covers a single oil instead of the three in 296, it includes a definite water content limit which the IEC version does not, and it omits the 'treatment' clause introduced into 296 in connection with the electric strength. The requirements in the British Standard include those shown in Table VII.

Mineral oil used in transformers to dissipate heat and also to act as insulant, is the main class of electrical insulating oil. The electrical property chiefly required of such an oil is high electric strength and, from this point of view, refining is less important than that the oil should be free of impurities such as undissolved water and fibres, the combined effect of which is far greater than that of either alone. For transformer oil a typical minimum electric strength of 200 kV/cm is normal at 50 Hz. This value refers to treated (i.e. dehydrated) oil in the breakdown type of test in the IEC specification and the 1972 revision of BS 148.

A simple test for free water is the 'crackle' test in which about 10 ml of oil

TABLE VII

Characteristic	Limit
Sludge value (max)	0.10%
Acidity after oxidation (max)	0.40 mg KOH/g
Closed flash point (min)	140°C
Viscosity, cSt at −15°C (max)	800 cSt
Viscosity, cSt at 20°C (max)	40 cSt
Pour point (max)	−30°C
Electric strength (breakdown) (min)	
Oil delivered in bulk	30 kV
Oil received in UK in drums	27 kV
Acidity (neutralization value) (max)	0.03 mg KOH/g
Corrosive sulphur	Non-corrosive
Water content (max)	
Oil delivered in bulk	35 mg/kg
Oil received in UK in drums	50 mg/kg
Density at 20°C (max)	0.895 g/cm^3
Dielectric dissipation factor at 90°C (max)	0.005

is placed in a dry test-tube and heated in a silent flame, absence of crackle indicating no substantial amount of water in suspension.

The specific heat of all mineral oils is similar, about 0.45, so that this factor can be neglected in the choice of an oil to meet the heat dissipation requirement. Cooling is frequently effected by convection, although pump circulation is also used, efficiency being governed mainly by the viscosity of the oil. Although only a maximum viscosity is laid down in most specifications, a lower limit is automatically enforced by inclusion, for safety reasons, of a minimum flash point.

A maximum density is included in many transformer oil specifications to ensure that, in very cold conditions, when a transformer is shut down it would not be possible for any ice to float on the oil; the IEC maximum density of 0.895 at 20°C means that a temperature below about −20°C would need to be reached before the density of the oil exceeded that of ice. Further requirements of a transformer oil are low pour point, to cover the contingencies of climatic variations, and freedom from corrosive sulphur compounds. Compliance with the latter is readily checked by inspecting for stains a piece of polished copper strip which has been immersed in the oil at an elevated temperature; the IEC specification stipulates 19 h at 140°C in a nitrogen atmosphere (i.e. ASTM method D 1275); some national specifications require a corrosion test in which silver is used.

The increasing stresses at which modern transformers operate have caused attention to be directed to resistivity and dielectric dissipation factor of transformer oils, and some specifications stipulate values for these, e.g. the IEC stipulates dielectric dissipation factor (0.005 max at 90°C), whilst in Germany a minimum resistivity of 10^{13} ohm cm, and a maximum dielectric dissipation factor of 0.004 at 90°C, are laid down. These increasing stresses, which can approach those met with in power cables, have also directed attention to gassing properties of transformer oils. Gassing is discussed later in the section dealing with cable oils; the relevance of this phenomenon in transformer oil applications is still somewhat controversial, but some users stipulate a minimum aromatics content in the oil to ensure adequate gas-absorbing properties.

Life of an oil in service depends on its quality and the operating conditions. Normally fifteen years or more life is expected, during which time it is subjected to conditions conducive to deterioration, namely temperatures in the region of 70 to 90°C, although 'hot spot' temperatures can exceed 100°C, sometimes contact with atmospheric oxygen, although this is largely avoided in well-designed larger transformers, and contact with copper and iron, which are oxidation catalysts. Products of oil oxidation range from water and volatile aldehydes, ketones, and the lower organic acids, to high molecular weight condensation and polymerization products, some of which are oil-insoluble. The volatile compounds tend to condense on metal surfaces above the level of the oil and cause corrosion; water, acids, and peroxides attack the insulation and protective materials, such as cellulose, varnish, paint, paper, etc.; the polar compounds, water in particular, together with fibres from deteriorated insulating material, decrease the electric strength; reduced heat transfer results from accumulation of oil-insoluble sludge in the cooling ducts and on the core and windings. Reduction of heat transfer leads to overheating of the core and

windings which, even if it does not cause complete failure of the transformer, raises the temperature of the oil and further accelerates the oxidation process.

Acidity development is usually taken as an index of the end of the useful life of an oil; acidity values at which oil is withdrawn vary, but around 0.5 mg KOH/g is a fairly typical figure. Some users prefer to follow the rate of change of acidity, a sudden increase being regarded as a pointer to trouble, possibly in the form of a 'hot spot'. Cases have been reported where acidity has been allowed to develop to considerably greater values than 1 mg KOH/g without breakdown, but this is considered unwise practice. In addition to measurement of acidity, other tests, such as electrical resistivity, dielectric dissipation factor, interfacial tension, saponification value, etc. have been used to assess deterioration of oils in service. Acidity is still probably the main single criterion, although resistivity and dielectric dissipation factor are considered nearly as important by some users. Oxidation tests, such as for new oils, are now seldom carried out on oils in service.

Recently increasing attention has been paid to analysis by gas chromatography of gases dissolved in transformer oil in service. Such analyses can give useful warning of existing faults and of incipient trouble in the transformer.

Maintenance of electric strength is highly important, and the test for this is usually done as routine in the case of oil in large transformers. If, owing to the presence of water or other contaminant, a value below the permissible minimum is found the oil is filtered, preferably under reduced pressure, to restore the electric strength, although the chemical deterioration of the oil is not significantly affected by such treatments.

Oxidation stability of a new oil is usually quoted in terms of acidity developed and sludge which can be precipitated, after an accelerated laboratory oxidation procedure which involves heating the oil for a specified period in the presence of air or oxygen, with or without a catalyst. Table VIII indicates the diversity of national test methods. The publication of an international (IEC)

TABLE VIII

Transformer Oil Ageing Tests: Principal Features Used in Various Countries

Country	Hours	°C	Oxidant	Catalyst	Criterion
United Kingdom	164	100	Oxygen	Cu	Sludge, acidity
Australia	210	120	Oxygen	None	Saponification value, tar value
Canada	24	120	Air	Cu	No sludge, acidity, interfacial tension
Germany	140	110	Air (semi-static)	Cu	Saponification value, sludge, dielectric dissipation factor
Japan	75	120	Oxygen	Cu	Sludge, acidity
USA (ASTM D1313)	24	140	Oxygen 17.2 bar)	None	Sludge
USSR	(6) 14	120	Air	Cu + Fe	(Water-soluble acids) Sludge, acidity
International–IEC publication 74,* 1963	164	100	Oxygen	Cu	Sludge, acidity

* Also adopted in Belgium, France, Germany, Holland, Italy, Sweden, Switzerland, and the UK.

ageing test, and its inclusion in the international specification for transformer oils, is leading to the gradual disappearance of the various national oxidation tests. The main difficulty met with in attempts to standardize on a common procedure is the correlation of the results of laboratory oxidations with field tests which, of necessity, extend over periods of years in transformers of varying construction and loading. It was widely felt that the test temperature of 150°C in the 1959 edition of BS 148 was too high because of the possibility of reactions taking place which would not occur in service. A test temperature of 100°C to 120°C is preferable, but lower temperatures increase the length of time required to take the oil to a conveniently measurable level of oxidation, and such long test duration is less convenient from a practical point of view. Reduction in the oxidation time at lower temperatures can be achieved by increasing the surface area of metallic catalyst or by the use of oil-soluble catalysts; the latter approach can be criticized in that it assumes that all oils take copper and other metals into solution to the same extent; an oxidation test using oil-soluble copper and iron is prescribed in Sweden, where inhibited oils are generally in use. Frequently different stability tests will assign varying merit ratings to oils.

Oxidation tests intended for 'straight' oils are not usually suitable for inhibited oils. For the latter, in order to obtain an assessable extent of deterioration, a test of greater severity, i.e. longer duration, higher temperature, more catalyst, or a combination of all these factors, is necessary. A modification of the IEC test suitable for inhibited oils has been developed, the temperature being raised to 120°C, the area of metallic catalyst trebled and deterioration assessed by measuring volatile acidity developed as oxidation progresses.

Transformer oils are most readily refined from wax-free, naphthenic type distillates, because of the low pour point requirement. Solvent (e.g. liquid sulphur dioxide, phenol) refining is frequently used, but some feedstocks are more amenable to acid (sulphuric) treatment; a combination of solvent and acid refining can also be employed. Adsorption refining of specially selected feedstocks is also possible.

Hydrogen refining is a procedure which shows considerable promise; use of urea dewaxing can make the hitherto unsuitable waxy distillates a processable feed for insulating oil manufacture. Raffinates obtained from the solvent extraction or acid refining processes are given a light contacting with activated clay before final dehydration, which may be by further filtration, usually with vacuum. The latter is considered desirable since it removes, in addition to suspended water, dealt with by filtration, much of the dissolved water. To indicate the amount of the latter, a typical equilibrium figure for water solubility in new transformer oil is approximately 40 ppm at 20°C, but the water content is reduced to around 10 ppm or less in commercial dehydrating units. It is essential to prevent the ingress of moisture to bulk storage and transport vessels by the fitting of silica gel or similar type breathers.

As a broad generalization it may be said that oils which are refined to the optimum extent in respect of oxidation stability, a feature largely linked with aromatics content, do not show as good a response to oxidation inhibitors compared to more severely refined oils. The latter oils may not have as good a resistance to oxidation as less severely treated oils, but their behaviour as inhibited oils will be better. Hence refining should, ideally, be adjusted to the

type of final product desired, i.e. a straight or an inhibited oil, but the usual requirement that the base oil used in a inhibited oil must itself meet the relevant specification must be borne in mind.

In connection with the gassing aspect, increasing interest is being shown in the aromatic content of transformer oils.

Extension of the normal life of a transformer oil can be effected in a number of ways; among these may be listed reduction in access of air to the transformer, reduction in catalytic effects, reclamation of used oils, and use of oxidation inhibitors.

Contact of the oil with atmospheric oxygen can be minimized in service by the fitting of a conservator tank so that the expansion and contraction, which take place during load cycles, occur, effectively, in a confined space, i.e. in the auxiliary tank containing relatively cold oil. Only the small surface area of oil in such a tank is in contact with the atmosphere. Alternatively, complete nitrogen blanketing can be resorted to; this is more usual in the USA than in the UK. Improved service can also be obtained by the protection of materials of construction with paints, varnishes, etc., which are resistant to the action of oil and its oxidation products. In this way catalytic effects can be reduced.

Additive-containing transformer oils

The use of additives in low concentrations to retard oxidation has found considerable application in the petroleum industry. In the case of transformer oils, extensive tests have been carried out in the laboratory and in transformers, and the use of additive-containing oils can be advantageous. The following mechanism of oil oxidation is generally accepted. The first stage is the attack by oxygen on hydrocarbon molecules to form peroxides that then dissociate to free radicals, which act as initiators for chain reactions involving free radical and hydrocarbons. However, if a compound with a labile hydrogen atom which will compete with the hydrocarbon for the free radicals is introduced, and thus produces a relatively inactive radical, then the chain sequence will be broken and the overall reaction inhibited. Such compounds are known as anti-oxidants or oxidation inhibitors; they terminate chain reactions by donating an electron or hydrogen atom to the intermediate peroxy radical. Those used in transformer oils are usually amines or hindered phenols (of which 2,6-di-tertiary butyl *p*-cresol (DBPC) is by far the most widely used); in inhibiting oxidation they are slowly used up and confer stability for a limited time known as the induction period.

An alternative means for suppressing oxidation is by deactivating those metal catalysts, and particularly copper, which markedly accelerate oxidation. Since small amounts of copper are present in almost all used transformer oils the metal could react with peroxides to form radical chain initiators; it could also react with anti-oxidants to reduce or even destroy their efficiency. Such catalytic action of copper involves a reversible shift between the cuprous and cupric states. It is believed that nitrogen- and/or sulphur-containing hydrocarbons are the species that readily oxidize to form hydroperoxides, which in turn are capable of solubilizing copper and ultimately lead to oil degradation. A copper solubility test demonstrates that transformer oils from different crudes and/or refined by different methods vary considerably in their ability to

dissolve copper; specific chelating additives, preferably in combination with oxidation inhibitors, suppress dissolution of copper. The effect appears to be due to adsorption of the chelating agent on the surface of the copper metal, indicating that these compounds can act as 'catalyst passivators' as well as 'catalyst deactivators'.

It has been predicted, by accelerated laboratory tests using conditions which approach those in transformer oil service, that oils containing additives will give much longer service lives than do straight mineral oils, but the results in practical service in transformers throw some doubt on the value of such oils other than in units operating under severe loading, such as distribution and pole transformers. Transformer oils containing an oxidation inhibitor, especially di-tertiary butyl *para*cresol (DBPC) are widely used in the USA and on the Continent (especially Sweden), and it is claimed by some that its inclusion results in twice the service life or permits operating temperatures to be raised by about 10°C. Practical trials by other workers, however, indicated that the inhibited oils behaved no more satisfactorily than the corresponding uninhibited oil.

Most workers consider that the combination of oxidation inhibitor and metal passivators shows greater merit than the use of anti-oxidants alone. Long-term field experience, especially in Australia where these grades are widely used, and to a lesser extent in the UK, suggests that such oils are much more stable than uninhibited transformer oil. It is claimed that where ordinary oils on severe duty accumulated acidity at the rate of 0.2 mg KOH/g/year, the additive-containing grade deteriorates at one-tenth this rate, and with a corresponding improvement in terms of retention of electrical properties.

Reclaimed transformer oils

Reclamation of used transformer oil has been given considerable attention by some of the largest users. Procedures used consist essentially of a preliminary removal of suspended material, followed by removal, or attempted removal, of oxidation products, and finally dehydration and degassing. Suspended material and free water can be removed by filtration and centrifuging. Sulphuric acid and other chemical treatments have been described as being suitable for the re-refining stage; but generally, either percolation through or contacting with an adsorbent such as activated clay or alumina is used. The extra lease of life given to the oil naturally depends on its initial condition and the extent of the treatment given (two-stage contacting gives better results than one-stage), but frequently the most that can be expected from small units is an increase equivalent to half the expected life of the original newly refined oil. Treatment costs may also be comparatively high if small quantities are handled. For these reasons, and the fact that the cost of a new oil can be partly offset by the value of the used oil as fuel, the reclamation of used oils is only carried out by some large users. Complete reprocessing on a refinery scale by the oil supplier is a different matter and yields oil equivalent to new.

Most countries, including UK, have nationally recognized recommendations for the maintenance of insulating oils, and a new international code on this subject is being prepared by IEC.

Cable Oils

Mineral oils which are used as dielectrics for high-voltage cables can be divided into high- and low-viscosity grades. Rosin or polymerized hydrocarbons which may be waxes are usually blended into the high-viscosity oils used to impregnate paper lapped round the conductor. The impregnation process includes degassing and dehydration at temperatures in the region of from 105 to 130°C under vacuum of the order of 1 mbar. Low-viscosity oils are used to fill the longitudinal ducts provided in cables of the hollow-core oil-filled type. Surge tanks are connected to the cable at intervals of a mile or less, depending on the ground contours, so that a head of oil is always maintained in the cable with a view to preventing void formation or ionization in the dielectric, due to thermal change.

Properties common to all cable oils, irrespective of viscosity, are low loss tangent, high resistivity, resistance to decomposition under electrical stress, and resistance to oxidation; however, this last property is less important than in transformer oils, since cable oils operate in essentially anaerobic conditions. A thermal stability test is often specified by cable makers having regard to cable manufacturing conditions rather than to operating conditions in service.

Electrical energy dissipated in the oil is turned into heat, which raises the cable temperature. This in turn results in increased loss tangent, and unless thermal equilibrium between the cable and its surroundings is established fairly quickly, and at not too high a temperature, eventual breakdown could occur. It is, therefore, essential that a cable oil should possess a low loss tangent. Such an oil is produced by careful refining, with particular attention to the elimination of traces of polar materials such as alkaline earth soaps left after lime neutralization of acid-refined oil. The loss tangent, which is frequently referred to as power factor, is usually measured with a Schering bridge circuit used in conjunction with specially designed oil cells. Loss tangent increases approximately 70 per cent for every 10°C rise in temperature in the range from 60° to 100°C. This test requires specialized equipment, and the electrical quality of an oil is often assessed by d.c. resistivity measurement which can be made with electronic apparatus which is readily available commercially. A high-voltage cable oil should have a d.c. resistivity value of the order of 10^{15} ohm cm at 20°C.

The addition of suitably refined rosin to the cable oil has little effect on the loss tangent at the normal temperature of cable operation, namely, in the region of from 60° to 80°C. At higher temperatures the slope of the loss tangent/temperature curve increases.

An electrical property of importance in a dielectric is permittivity. A value of approximately 2.2 is typical for mineral oils; it may vary slightly (say in the range from 2.1 to 2.3) with oil composition, tending to rise with increasing oil density; the change of density of an oil with temperature is directly reflected in the permittivity.

Hydrocarbons, when subjected to high electrical stresses such as exist in an electrical cable, tend to evolve gas, predominantly hydrogen with traces of lower hydrocarbons; formation of highly polymerized material of a wax-like nature also occurs. Excessive evolution of gas can set up a pressure and distort the cable sheathing, and also form gas pockets inside the cable, which are much

less resistant to electrical breakdown than the oil itself. It has been found that oils from naphthenic-base crudes are much less prone to gas evolution than those from paraffinic crudes. Additionally, rosin, a highly unsaturated material which is blended into heavy cable oils, reduces gas-evolving tendencies and is more readily soluble in naphthenic than in paraffinic oils. In light cable oils, where rosin addition would be unsuitable, addition of aromatic hydrocarbons has a similar effect. Although pure compounds, e.g. naphthalene, have been used, it is customary to incorporate aromatic extract obtained from solvent refining processes. The gassing behaviour (absorption or evolution) of oil is determined under electrical stress (about 4 kV/mm) for about two hours in a hydrogen atmosphere. International agreement has been reached on a suitable test procedure which has been published by the International Electro-Technical Commission, Publication Number 628. An equivalent test is described in BS 5797. Indication of unsaturation and aromaticity in terms of iodine value and aniline point has been specified, but these are not satisfactory pointers to gassing behaviour; i.r. and u.v. spectroscopy are, however, useful guides to oil constitution in this context and, for production control of a given oil, u.v. absorption can be correlated with gassing properties.

Oxidation of an oil increases its polar character and hence its loss tangent. Oxidation stability of a cable oil is normally assessed by loss tangent increase after laboratory oxidation under either static or dynamic conditions. The oxidation is often carried out in the presence of polished copper wire which acts as a catalyst for the oxidation process, and at the same time, by visual examination of the state of the copper at the end of the oxidation period, provides a check on freedom of the oil from corrosive sulphur compounds. Addition of rosin to heavy cable oil, and aromatic extract to the light grade, enhances oxidation stability. In the latter case, the increase in stability is probably due to the inhibiting effect of the aromatics when these oxidize.

Cables are often laid in exposed conditions, and oils for hollow-core cables should have low pour points, below $-40\,^{\circ}C$. High-viscosity oils used for impregnation of solid type cables should have a low viscosity index so that they are viscous at the operating temperature and yet free-flowing at degassing and impregnating temperature. Addition of rosin further decreases the viscosity index.

Cables are sometimes manufactured in which the dielectric is maintained under a gas pressure of the order of 15 bar, with the object of preventing ionization in gas pockets. Such design allows of satisfactory operation at higher stresses and temperatures than those pertaining in certain other types of cables. The mineral oil component of such pressurized cables is usually blended with a polymer, such as polyisobutene. Attention has also been given to the effect of the cable impregnant on the ability of cables to withstand high voltage transients caused through lightning strikes on associated overhead lines, and by switching operations. The impulse electric strength of cable oils is of interest in this connection.

Switch Oils

Refined mineral oils are used in circuit-breaking equipment to interrupt and quench the arc formed between moving parts, and to act as an insulant.

Although coolant effect is required only at such times as the switchgear is actuated, a low-viscosity oil such as a transformer oil facilitates rapid dispersal of the decomposition products formed by arcing, and this oil is normally used. Pour point depressants are sometimes included to ensure satisfactory operation of the equipment at low ambient temperatures. Carbon is the main decomposition product and the electric strength of the oil has to be maintained by periodic filtration. A further problem is that of deposition of carbon on insulators, and attempts have been made to minimize this effect by coating the insulators with materials which will repel the carbon. Adhesion to the insulators and insolubility in oil are necessary requirements of such coatings.

Capacitor Oils

Refined mineral oil is used as an impregnant for paper insulation of capacitors and as such is a dielectric, not mainly a coolant; a low loss tangent is, therefore, an essential requirement of oil for this application. High electrical resistivity, resistance to decomposition under electric stress, and resistance to oxidation are also desirable properties. The viscosity requirement is similar to that for hollow-core cable oils. Oils specially treated to give low loss tangent, are generally used, although in this market synthetic oils have displaced mineral oils to a very great extent.

PROTECTIVES

It is largely owing to the availability of iron and steel that our civilization has been able to make the great advances of the last 200 years—without them we should certainly be condemned to a life of perpetual mediaeval primitiveness without all the advantages which have accrued from the advanced technology of the twentieth century. It is most unfortunate, therefore, that these most versatile materials, upon which we depend so much, suffer one major weakness, in that they are subject to corrosive attack under the climatic conditions prevailing over much of the globe.

The devising of means to prevent the inexorable decay of iron and later steel artefacts is a subject which has occupied men's minds ever since the first iron age blacksmiths smelted ironstone to forge primitive spearpoints some 5000 years ago. From the limited metallurgical skills of these itinerant artisans has grown a world iron and steel industry with an annual output of some 1 220 million tonnes, and it comes as no surprise, therefore, that a parallel evolution from the esoteric art of the alchemist has led to a whole industry devoted to the protection from corrosion of everything from panel pins to ocean liners.

A legion of protective schemes is available, falling into the following categories:

(a) Metallic: plating, galvanizing, tinning,
(b) Organic: plastic coatings, paints, powder coatings, and protectives,
(c) Miscellaneous: vitreous enamelling, aqueous inhibitors, impressed current cathodic protection.

Each of these methods has its strengths and weaknesses, and particular applications for which it is ideally suited. In many cases treatment costs per

article are high, and can only be justified on consumer items where protective power is combined with the customer appeal of a decorative finish. For the great majority of engineering work, in applications where the emphasis is on a purely functional system, temporary protectives based upon petroleum products gain the ascendancy, owing to their ease of application and removal, and, above all, their comparative cheapness. The significance of the adjective 'temporary' lies not so much in any implication of the length of protection which they may afford, but in the fact that products of this type are designed to be easily removed before the protected component is pressed into service (although often an apt choice of grade will obviate this operation). Indeed, a wide range of products is available to give protection varying, according to composition, from a few days in good storage conditions to several years in quite hostile environments.

Composition

In general, temporary protectives comprise a basic film-forming material, a combination of additives and a solvent. The film-forming material may be oil, petrolatum, wax, bitumen or a resin, or almost any combination of these. It determines the consistency of the film, serves as a carrier for the additives, and has also to some extent an inherent water repellency which contributes to the protective properties of the product.

The choice and balance of the additives is determined by the function the product is intended to perform. Of primary importance are the anti-corrosion additives, at least one of which is present in all but the shortest term protectives. Traditionally this function was performed by petroleum sulphonates and lanolin, by-products of the manufacture of white oil and wool, respectively. The increasing use of synthetic fibres in place of wool, and the advent of hydrogenation techniques for white oil production have led to considerable fluctuations in quality and availability of these materials, and they have now been largely supplanted by a multitude of synthetic substitutes. Most prominent amongst these are oxidized wax and petrolatum derivatives, synthetic sulphonates, and synthetic esters. A variety of other additives may be present, and these will normally be ascribable to the following classes:

Fingerprint neutralizers
Water-displacement additives
Plasticizers
Anti-oxidants/stabilizers
Rheology modifiers

The solvent is usually of the hydrocarbon type, since such materials are very favourable on the grounds of cost, but the traditional white spirit is losing ground to narrow-cut special boiling point fractions, which combine a high flash point with rapid evaporation. The lower toxicity halogenated solvents are also encountered occasionally, where their short drying times and non-inflammability can compensate for their high cost. Current preoccupation with health and safety has led to the limited use of low aromatic content naphthenic condensates, and also given a new lease of life to protectives applied in the form of an aqueous emulsion. There is no doubt that health, environmental,

and cost considerations will result in further expansion of the market held by the latter, although the day when solvent-based protectives will join the dodo is still very distant. A final group of products, including inhibited oils, greases and hot-dip compounds, contain no solvent at all.

Classification

As can be seen from the foregoing, the number of possible combinations is almost limitless, and it becomes essential to adopt a simple classification system. This is provided in a serviceable if imperfect form by British Standard 1133 Section 6, which affords a good introduction to the field of temporary protectives, with detailed coverage of their selection, testing, and practical usage. It groups products into the following types:

Type TP 1. Hard-film, solvent-deposited protectives, based usually on resins, bitumen or wax in a volatile solvent, and generally applied by dipping or spraying. On evaporation of the solvent, a thin hard protective film remains. There are three grades:

TP 1a quick drying
TP 1b slow drying
TP 1c slow drying with water-displacing properties.

Type TP 2. Soft-film, solvent-deposited protectives, based commonly on petrolatum and additives in a volatile solvent, and applied by dipping or spraying. On evaporation of the solvent, a thin soft protective film remains. There are two grades:

TP 2a ordinary grade
TP 2b water-displacing grade.

Type TP 3. Soft-film, hot-dip protectives, normally based on petrolatum, applied by dipping into the molten product.

Type TP 4. Soft-film protective greases applied by brushing or smearing to give a thick soft film. There are two grades:

TP 4a mineral oil based grease
TP 4b castor oil based grease.

Type TP 5. Soft-film, semi-fluid compounds, usually based on petrolatum in mineral oil, and applied by brushing or swabbing to give films of medium thickness.

Type TP 6. Oily film products consisting of inhibitors in mineral oil, applied by dipping, spraying or flushing, and often serving as a lubricant as well as a protective. There are two grades:

TP 6a general purpose protective oils
TP 6b engine storage oils.

Type TP 7. Strippable hot-dip coating consisting of ethyl cellulose and mineral oil, together with plasticizers, stabilizers, and anti-oxidants. It is applied by hot-dipping to form a tough impermeable film which can readily be stripped from the protected article.

Type TP 8. Solvent-deposited strippable coating usually consisting of a vinyl copolymer resin with various additives in a volatile solvent, and applied by brushing, dipping or spraying, to form a tough impermeable film which can readily be stripped from the protected article.

Type TP 9. Volatile corrosion inhibitors, the vapour of which will inhibit corrosion of ferrous metals.

Type TP 10. Contact inhibitors which, when in contact with metallic surfaces, will inhibit corrosion.

Choice

A wide variety of factors must be taken into account when choosing a protective scheme for a given application, to ensure that it is capable of affording the required degree of protection, compatible with all the materials and functions of the system, and suitable for use with the application and removal methods available. The main points to be considered are:

1. The period of protection required. Where components are held in storage for variable periods, the optimum would be a product to cover the longest probable term of storage. Frequently, however, it is necessary on economic grounds to pick a product which will give an adequate duration of protection for say 90 per cent of stored components, the slowest moving 10 per cent being retreated after a suitable period.

2. The conditions of storage which the protective coating must withstand. The variation in degree of severity of different environments can be considerable. In a store where the humidity is maintained below 50 per cent, the rate of corrosion of bare mild steel is scarcely perceptible, but increase the humidity to 80 per cent and add airborne industrial pollutants, and the rate can increase by two orders of magnitude. For deck cargo in the tropics, subject to high humidity and sea-water spray, a further fivefold rate increase can be observed. Clearly then, a careful assessment must be made of all the factors which will contribute to the corrosive potential of the environment.

From a consideration of 1 and 2, one can determine the degree of performance required of the product.

3. The geometry and complexity of the work to be treated.

4. Whether the protected components will be subject to manipulation during storage.

5. Whether the protective coating is to be removed eventually, and, if so, what means are available to effect this.

A critical analysis of 3, 4, and 5 will indicate the most suitable consistency for the film material. The softer it is, of course, the easier will be its eventual removal, but equally the more liable it is to accidental erosion during handling. Oily films are much the most suitable for mechanisms with moving parts, but, because of the thinness of film, are often unavailable in a sufficiently high-powered form to withstand arduous storage conditions. They tend also to pick up dust, thereby necessitating removal which might otherwise have been avoided. All these points must be taken into account when deciding upon the character of the film.

6. What limitations are placed on the means of application.

Solid films must be applied either above their melting point or by solvent deposition, and both of these methods have their advantages and shortcomings. Hot-dip application involves capital expenditure and operational costs on heating equipment. Large items can be protected by hot brushing but this is laborious. Hot spraying is possible but little used owing to the high capital cost of suitable spray equipment. Solvent deposition on the other hand offers none of these problems, but has the disadvantage that protected components must be allowed to stand until the solvent has evaporated fully. The faster evaporating hydrocarbon solvents have low flash points, and this can present problems. Replacement with non-inflammable halogenated solvents involves considerable extra cost, and also toxicity problems in poorly ventilated work areas. The use of high flash point solvents in combination with forced drying involves once again the capital and operational costs of the drying equipment.

7. Whether water-displacing properties or any other special characteristic is required.

A wide variety of solvent-deposited protectives is available with specially selected wetting agents incorporated in the formulation to lower the interfacial tension with water. They are thus enabled to displace water from the surface of dipped components. The displaced water accumulates at the bottom of the dipping tank, whence it is drained at regular intervals. Since the final operation in the manufacture of a wide variety of items is washing to remove cutting oil traces, this ability to displace water is particularly valuable. Unfortunately products with more than about 40 per cent solids generally make unsatisfactory water-displacing fluids, so that this property is not available with the very long-term, high solids content type of protective. Certain low-viscosity inhibited oils also have water-displacing powers, but these are not widely used since they tend to suffer from emulsification troubles unless used very carefully.

Several other special properties are available in temporary protectives of various kinds. These include: suitability for electrostatic spray techniques, fingerprint neutralizing properties, thixotropic rheology characteristics, compatibility with various plastics and elastomers, and ability to accept a subsequent coat of paint.

Usage

Provided the following simple rules are observed, the use of temporary protectives is simplicity itself.

1. Always apply to a clean surface. The presence of dirt or contamination on a protected product can seriously curtail its storage life. Soluble or straight cutting oils, chemical cleaners or residues from welding fluxes, liquid salt baths or pickling baths can each cause outbreaks of corrosion when incompletely removed from manufactured articles.
2. When using a product containing a volatile solvent, ensure that the dip tank is properly covered during periods of disuse to minimize evaporation losses. Products containing exceptionally volatile solvents such as trichloroethane should be subject to a periodic check on solids content, and fresh solvent added if necessary.

3. Articles treated with a solvent-deposited protective should be allowed to stand for sufficient time to allow the solvent fully to evaporate. This is of particular importance where they are subsequently to be enclosed in sealed packages, since evaporating residual solvent can recondense to give a vapour-degreasing effect.

4. When using water-displacing fluids, do not agitate work during immersion to expedite water displacement, since this can result in emulsification of the displaced water in the fluid, and thus drag-out of water on dipped components. Fluids containing a small amount of insoluble material, such as lanolin solutions, should be stirred gently at the beginning of a shift. Provided that the dipping tank is in fairly frequent use, the agitation provided by the dipping action will then be adequate to maintain the solids in a state of dispersion.

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Quality Assessment

By L. H. BELL

INTRODUCTION

The assessment of the quality of petroleum products is of major concern not only to the refiner and marketer, but also to the user who may be a direct consumer or a manufacturer whose products incorporate petroleum products.

To assess this quality, tests are carried out on the products and the results of the tests are checked against relevant specifications. A simple specification would be one against which only a few limiting parameters would require testing. This could be the case if the same crude oil was refined by the same process to produce a particular product. However, in the present day, there are many different crude oils and equally many different processes for manufacturing a particular product. As a result specifications are not simple but contain many parameters, and in many cases these parameters are interrelated, for example front-end volatility, flash point, and vapour pressure.

Further, because of the trend over the past few years to conserve oil the limits of the parameters in the specifications have been pared considerably. As a consequence the test methods used in assessment are being continually examined in an endeavour to improve the precision, and where modern and improved testing equipment is available to change the method.

In this chapter the test methods used in assessing the product quality will be reviewed in their various classes—empirical, chemical, physical, and mechanical rig tests. Mention will be made of the current state of 'in-line' testing. Whilst no special mention will be made regarding sampling of petroleum materials for examination its importance cannot be over-emphasized. The results of analysis of any material are meaningless unless the appropriate sampling has been carried out and the final sample(s) duly labelled with all relevant information.

The majority of tests quoted are to be found in the Institute of Petroleum's publication *IP Standards for Petroleum and its Products*, formerly published in four parts. Current status is as follows:

Part I, Volume 1, Methods for Analysis and Testing, 1–230, 41st Edition, 1982.

Part I, Volume 2, Methods for Analysis and Testing, 231–359, 41st Edition, 1982.

Part II—Manual for Rating Fuels by the Research and Motor Methods, now discontinued. As all of these methods are jointly agreed by ASTM and IP the publication issued by ASTM as Part 47—Test Methods for Rating Motor, Diesel and Aviation Fuels is now accepted.

Part III—Methods for Assessing Performance of Engine and Automotive Transmission Lubricants—Engine and Axle Tests—all methods with the exception of the Caterpillar Supercharged Test, IP 231, have been adopted

and published as CEC Standard Methods of Test by the Coordinating European Council for the development of performance tests for lubricants and engine fuels.

Part IV—Methods for Sampling, 4th Edition, 1976, contains manual methods of sampling. Frequently samples are drawn from pipeline streams using automatic sampling equipment and for this purpose reference should be made to the IP Petroleum Measurement Manual Part VI, Section 2, Tentative Procedure for Automatic Sampling of Liquids from Pipelines.

Identical or equivalent test methods are also available in the American Society for Testing and Material's publication *ASTM Standards,* published annually:

Part 15—Road and Paving Materials; Bituminous and Polymeric Materials for Highway Construction, Waterproofing and Roofing, and Pipe; Skid Resistance.

Part 23—Petroleum Products and Lubricants (I) D56–D1660.

Part 24—Petroleum Products and Lubricants (II) D1661–D2896.

Part 25—Petroleum Products and Lubricants (III) D2891–latest; Aerospace Materials; Catalysts.

Part 39—Electrical Insulation—Test Methods: Solids and Solidifying Fluids.

Part 40—Electrical Insulation—Specifications: Solids, Liquids and Gases; Test Methods: Liquids and Gases; Protective Equipment.

Since 1963 many methods have been standardized as joint ASTM/IP Methods, and the 1982 edition of *IP Standards* contains 73 joint methods.

Identical methods taken from the IP Standards that are needed for Product Specifications are also published by the BSI as parts under their BS/2000 series. Thus BS 2000: Part 230: 1982 is identical with IP 230/81.

EMPIRICAL TEST METHODS

These represent about one-third of the test methods in current use and are concerned with a variety of properties or characteristics which may be listed as follows: stability, corrosion, flammability, melting, viscosity, constitution, and volatility, together with a few that cannot easily be classified.

Generally none of them measure any precise fundamental property, either chemical or physical, but in most instances their value lies in providing a quick, easy, and reasonably inexpensive means whereby quality may be assessed. Many tests have been devised to satisfy a particular product requirement.

STABILITY TESTS

Methods for the evaluation of storage stability and resistance to oxidation have been devised for (a) motor and aviation fuels, (b) lubricating, turbine, and transformer oils, (c) grease, and (d) emulsions as follows:

(*a*) *Motor and aviation fuels*

IP 40/82.* Oxidation Stability of Gasoline (Induction Period Method).
IP 131/77. Existent Gum in Fuels by Jet Evaporation.
IP 138/82. Oxidation Stability of Aviation Fuels (Potential Residue Method).
IP 323/81. Thermal Oxidation Stability of Turbine Fuels.

Method 131 is suitable for all types of volatile fuel. Method 40 provides a measurement of oxidation stability of gasoline by measurement of oxygen absorption. Method 138 makes a similar evaluation for aviation fuels by estimation of the gum left after a period of oxidation; the method is slowly going out of use. Method 323 has replaced the now obsolete Method 197, and is a relatively easier method using less product for the evaluation of the tendency of the aviation fuel to deposit decomposition products in the fuel system.

(*b*) *Lubricating, turbine, and transformer oils*

IP 48/80. Oxidation Test for Lubricating Oil (200°C with air for 2 × 6 h).
IP 229/73 (reapproved 1980). Oxidation Stability of Steam Turbine Oils by Rotating Bomb (150°C with oxygen at 90 psi).
IP 280/80. Oxidation Stability of Inhibited Mineral Turbine Oils (120°C with oxygen for 164 h in the presence of soluble metal catalysts (iron and copper)).
IP 306/82. Oxidation Stability of Straight Mineral Oil (120°C with oxygen for 48 h with (a) no catalyst and (b) solid copper catalyst).
IP 307/80. Oxidation Stability of Mineral Insulating Oil (100°C with oxygen for 164 h with solid copper catalyst).
IP 328/80. The Assessment of the Oxidation Stability of Mineral Turbine Oils During Use (150°C with oxygen).
IP 335/80. The Oxidation Stability of Inhibited Mineral Insulating Oils (120°C with oxygen for 236 h or period dependent on development of a volatile acidity, with solid copper catalyst).

The oxidation propensities of lubricating, turbine, and transformer oils is a matter which, over the years, has received much attention. Since the previous edition (ten years ago) three tests have been made obsolete, but four new tests have resulted. This means that there are seven tests, all of the same fundamental character, namely contact with oxygen at elevated temperatures for varying periods of time and mostly with catalysts. None of these seven tests has been definitely related to performance in use, but they are available to the manufacturer for the control of quality from batch to batch.

Method 48 is not suitable for additive-type oils. Method 229 employs expensive apparatus, but may be regarded as a rapid means for estimating the stability of new turbine oil or for assessing the remaining stability of oils in service. Methods 306, 307, and 335 use similar apparatus to Method 280, but different conditions. Method 306 is used for straight (plain) mineral oils,

* The figure after the Standard Number indicates the year in which the method was adopted or was last revised. Where methods have not needed revision for several years, but have been studied and reapproved, the year of reapproval is indicated.

Method 307 for insulating oils, and Method 335 for inhibited insulating oils. Method 328 uses an electrolytic cell to supply oxygen used up in the test.

(c) Grease

Stability tests for grease are not numerous but provide useful means of controlling manufacture and quality. They are specific in scope as will be appreciated from the following titles.

IP 121/75 (reapproved 1981). Oil Separation on Storage of Grease.

IP 142/74 (reapproved 1980). Oxidation Stability of Lubricating Greases by the Oxygen Bomb Method.

IP 180/62 (reapproved 1981). Heat-stability of Calcium-base Greases.

IP 266/78. Rolling Bearing Grease Churning Test.

(d) Emulsions

IP 263/70 (reapproved 1979). Emulsifiable Cutting Oil Emulsion Stability.

IP 290/73 (reapproved 1980). Emulsion Stability of Water-in-oil Emulsions at Ambient Temperature.

IP 311/74 (reapproved 1981). Thermal Stability of Emulsifiable Cutting Oils.

Method 311 uses Method 263 following storage of samples at 0 and 50°C.

CORROSION TESTS

Most crude oils are corrosive to a greater or lesser extent, frequently owing to the presence of sulphur compounds, organic acids and traces of brine left after settling, and care therefore needs to be taken to ensure that any such material carried forward during the processing of the oil is completely removed. Means are therefore required to evaluate the corrosive potentialities of petroleum products, and these are designed with due regard to the conditions of use. All of the following ten methods are essentially practical in character, and in general comprise visual evaluations of the corrosive effect on metals, except for Method 178 which is concerned with the effectiveness of corrosive coating and Method 331 where volatile acids, deposit, and viscosity change are checked.

IP 112/56 (reapproved 1981). Corrosive Substances in Grease Copper Strip Test. (Time dependent on specification, temperature dependent on dropping point of sample.)

IP 125/82. Aqueous Cutting Fluid Corrosion of Cast Iron. (Time 24 h, temperature 18.5°C, humidity 52%.)

IP 135/64 (reapproved 1981). Rust-preventing Characteristics of Steam-turbine Oil in the Presence of Water. (Advised time 24 h—can be varied—temperature 60°C, steel specimen.)

IP 154/78. Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (general test for fuels, conditions vary according to product).

IP 178/74 (reapproved 1981). Temporary Corrosion Preventives Water Displacing and Corrosion Protection Properties. (Time 72 h, room temperature, high humidity, steel panels.)

IP 227/82. Silver Corrosion by Aviation Turbine Fuels. (Time four hours, or longer, temperature 50°C.)

IP 293/73 (reapproved 1980). Ferrous Corrosion—Prevention Characteristics of Gear Oils in the Presence of Water. (After pretreatment, time seven days, temperature 52°C, humidity 80%, both ferrous corrosion and copper strip corrosion reported.)

IP 315/74 (reapproved 1981). Corrosive Sulphur in Electrical Insulating Oils. (Time 19 h, temperature 140°C, copper strip used.)

IP 329/79. Corrosive Properties of Water-based Hydraulic Fluids. (Time 330 h, temperature 50°C, variety of metals.)

IP 331/82. Stability—Corrosion Test for Non-Aqueous Fire Resistant Fluids. (Time 164 h, temperature 120°C.)

FLAMMABILITY TESTS

The flammability of petroleum products may be measured by the determination of flash point, either closed or open, or by fire point.

Flash point methods are:

IP 33/59 (reapproved 1978). Flash Point by the Abel Apparatus Petroleum (Consolidation) Act 1928 Method.

IP 34/82. Flash Point by Pensky–Martens Closed Tester.

IP 113/53 (reapproved 1981). Flash Point (closed) of Cutback Bitumen.

IP 170/75 (reapproved 1981). Flash Point by the Abel Apparatus.

IP 303/81. Rapid Tests for Flash Point.

IP 304/80. Flash Point Using the Cup of any Standard Closed Cup Apparatus.

Method 33 is a UK statutory requirement related to the storage of volatile flammable liquids. Method 34 is applicable to high flash point materials such as lubricants, gas oils, and residual fuels, whilst Method 170 covers the range—18 to 71 °C. Both Methods 34 and 170 are considered non-equilibrium in that a test flame is inserted into the vapour space of the test material at regular temperature intervals, thus slightly changing the composition of the product. However, both methods are well established and lend themselves readily to automation.

Methods 303 and 304 are considered equilibrium in that one flame application is applied to the product under test at a specific temperature. Thus they are basically go/no go type tests. Method 304 uses any closed cup, but is rather tedious. Method 303 is an extremely useful field test in that the apparatus is portable, the elapsed time for a test is very short (a matter of a few minutes), and the amount of sample is small (2 ml).

As far as open flash and fire points are concerned the following:

IP 35/63 (reapproved 1981). Flash Point (OPEN) and Fire Point by Means of the Pensky–Martens Apparatus.

IP 36/67 (reapproved 1981). Flash and Fire Points by Cleveland Open Cup

have been questioned regarding their usefulness as pointers to hazardous situations. At this time there is still the opinion, particularly for roofing bitumen, that there is a need for the methods.

Finally, mention should be made of ASTM Method E659 which is a test for the auto-ignition temperature of liquid chemicals, and which in spite of its complexity can give information to cover special conditions of storage and use.

VOLATILITY TESTS

Volatility is assessed by three groups of procedures: distillation, vapour pressure, and loss on heating, namely:

Distillation

IP 23/68 (reapproved 1979). Dilution of Gasoline—Engine Crankcase Oils.
IP 24/79. Distillation of Crude Petroleum Preliminary Distillation.
IP 27/74 (reapproved 1981). Distillation of Cutback Asphaltic (Bituminous) Products.
IP 78/79. Distillation of Crude Residue.
IP 123/82. Distillation of Petroleum Products.
IP 191/65 (reapproved 1981). Distillation of Natural Gasoline.
IP 195/81. Distillation Range of Volatile Organic Liquids.

Vapour pressure

IP 69/78. Vapour Pressure--Reid Method.
IP 161/73 (reapproved 1980). Vapour Pressure—Liquefied Petroleum Gases.

Loss on heating

IP 45/58 (reapproved 1981). Loss on Heating—Bitumen and Flux Oil.
IP 183/79. Evaporation Loss of Lubricating Greases.

All the distillation methods listed are simple, both as regards apparatus and procedure; they embody no fractionation, but their limitations are well known and understood. With the exception of Method 23, all involve distillation from a 'side-arm' flask, and the yields of distillate at certain vapour temperatures are recorded. It will be seen that most distillation methods have specific uses.

Method 123 is perhaps one of the most used of all petroleum tests, but because the thermometer employed is standardized at total immersion, the boiling points or ranges determined on a sample bear no accurate relationships with true boiling points. The view is held in some quarters that this disability could be overcome by the use of thermometers standardized at the appropriate partial immersion, but on the other hand it is claimed that the results of distillation tests do bear a close relationship to the yields obtained from refining plant.

There are some very good automatic apparatuses that are accepted for use with Method 123.

The conditions under which vapour pressures are determined give results which are not 'true' because of the air which is unavoidably present in the apparatus. The two best, Methods 69 and 161, employ similar apparatus and

procedures, and provide results which are meaningful to the petroleum industry. There is, however, another procedure (Vapour Pressure—Micro Method—IP 171) which provides results more closely approaching true vapour pressures, but by correlation gives results regarded as Predicted Reid Vapour Pressure. This method is mentioned under the heading Physical Test Methods, p. 1126.

The two tests which cover loss on heating are essentially empirical in nature; they are simple in concept and provide useful means for the control of production and quality. The results will rarely provide an accurate prediction of behaviour in use or storage.

Viscosity Tests

Empirical tests for the assessment of the viscosity of viscous materials may be listed as follows:

IP 72/58 (reapproved 1981). Viscosity—Cutback Bitumen and Road Oil.
IP 212/75 (reapproved 1981). Viscosity—Bitumen Road Emulsion.
IP 49/79. Penetration of Bituminous Materials.
IP 50/69 (reapproved 1979). Cone Penetration of Lubricating Grease.
IP 179/79. Cone Penetration of Petrolatum.
IP 310/75 (reapproved 1981). Cone Penetration of Lubrication Grease Using One-quarter and One-half Scale Cone Equipment.
IP 58/82. Softening Point of Bitumen Ring and Ball.
IP 230/81. Pumpability Test for Industrial Fuel Oils.

Methods 72 and 212 are applicable to viscous liquids; they involve the measurement of efflux time when the material is allowed to flow vertically downwards at a controlled temperature through a standardized orifice. Although they do not give results in fundamental units, they have the advantages of simplicity and low-cost apparatus.

With highly viscous materials, recourse can be made to penetration tests in which the vertical penetration of a loaded needle or cone into the sample for a period of time provides a practical assessment of viscosity. Method 310 is intended for use only where the size of sample limits the use of Method 50.

The determination of the softening point of bitumen is regarded by some as an indication of viscosity, although from the point of view of the application of bitumen its use is limited to that of its title.

Method 230 is based on viscosity, and results show the temperature at which a residual fuel oil should be maintained (a) for handling purposes and storage where no outflow heater is fitted, and (b) for storage where an outflow heated is fitted.

Liquefaction and Solidification Tests

The tests designed to ascertain the tendency of certain petroleum products to melt or liquefy, to solidify or to precipitate wax-like materials are:

IP 31/66 (reapproved 1981). Drop Point of Grease.
IP 76/70 (reapproved 1978). Congealing Point of Petroleum Waxes, including Petroleum.

IP 132/80. Dropping Point of Lubricating Grease.
IP 133/79. Drop Melting Point of Petroleum Wax, including Petrolatum.
IP 15/67 (reapproved 1981). Pour Point of Petroleum Oils.
IP 16/73 (reapproved 1980). Freezing Point of Aviation Fuels.
IP 219/82. Cloud Point of Petroleum Oils.
IP 309/80. Cold Filter Plugging Point of Distillate Fuels.

A particular test which could be allocated to this group is IP 80/53 (reapproved 1981) Breaking Point of Bitumen Fraass Method, which determines the temperature at which a bitumen becomes sufficiently brittle to fragment on distortion. The phenomenon is not, however, attributable to the presence or absence of oil or wax, but rather to the chemical structure of the bitumen.

Tests for melting or liquefaction

The first four tests in the above list measure the same property, either the temperature at which a sample melts sufficiently for a drop to fall or the solidification temperature of a liquid sample adhering to the bulb of a thermometer.

Solidification and Precipitation Tests

Pour point is a well-established test which does what its title suggests, namely, it estimates the temperature at which a sample of oil becomes sufficiently solid to prevent its movement by pumping. When considering the results, however, it must be borne in mind that the pour-point temperature depends to a large extent on the thermal history of the sample.

Two of the methods (16 and 219) are concerned with the temperature at which crystals of solid hydrocarbons appear when the sample is cooled. This information is important when fuel filters are in use at low temperatures (e.g., in aircraft), and when clogging of the filters would stop the flow of fuel to the engine. Method 309 is used to determine the extent to which diesel fuel or gas oil will flow, even though the temperature is below that at which wax crystals normally appear, i.e., Cloud Point.

Calculations

Methods of calculation are available whereby an indication of certain 'behaviour' properties may be obtained from characteristics such as aniline point, volatility, density, sulphur and hydrogen content. Current methods are:

IP 21/53 (reapproved 1981). Diesel Index.
IP 218/81. Calculated Cetane Index of Diesel Fuels.
IP 193/73 (reapproved 1980). Estimation of Net Heat of Combustion of Aviation Fuels (Aniline Gravity Method).
IP 355/82. Estimation of Net Heat of Combustion of Aviation Fuels (Hydrogen Content/Density Method).

Method 21 provides an indication of the ignition quality of diesel fuel and

requires knowledge of the density and aniline point (IP 2), the latter being a measure of aromaticity. The method is little used today.

Method 218, as its title implies, provides a means for estimating the cetane number of diesel fuel when a test engine is not available for the determination of cetane number (IP 41 Ignition Quality of Diesel Fuels). It necessitates determinations of API gravity and mid-boiling point of the sample.

Currently doubt has been cast on the validity of this equation and ASTM have produced a mathematical equation, still based on API gravity and mid-boiling point, that it is maintained predicts cetane number for today's diesel fuels more accurately than the formula in Method 218. Work carried out by IP Panels ST-L-1 and ST-B-1 indicates that the new formula is good for fuels with cetane numbers in the 40–55 region, whilst the old formula is more valid for fuels with cetane numbers above 55. The basic difficulties in predicting cetane number are: (1) the poor precision of IP 41, Ignition Quality of Diesel Fuels; (2) the numerous different types of diesel fuel available which are dependent on crude oil source and manufacturing process; (3) whether ignition promoters have been added to the diesel fuel.

Methods 193 and 335 are only applicable to aviation fuels and are used as a guide when it is not possible to make an actual determination of calorific value, IP 12. The calculation in Method 193 is based on API gravity, aniline point, and sulphur, whilst Method 355 is based on hydrogen content, density, and sulphur.

In addition to the above, mention should be made of the Characterization Factor[1] which is the cube root of the average boiling point (in degrees fahrenheit absolute) divided by the specific gravity at 60 °F. These factors are additive; they are higher for paraffins than for naphthenes and aromatics, and increasing branching raises the factor except for low-boiling paraffins. Characterization factors cannot be used to distinguish between mixtures of paraffins and aromatics, and mixtures of naphthenes.

Since the earlier edition, work on producing mathematical formulae from as few basic variables as possible, with a view to using the predictions in specifications, has been carried out to a limited degree. However, there is a seemingly great reluctance to use these predicted numbers in specifications. Work is continuing under the IP Method Evaluation Sub-Committee in this area, the above Method 355 being the latest output.

Miscellaneous Tests

The following remaining empirical tests cannot easily be allocated to any of the seven sections dealt with above; nevertheless they are all in current use and provide useful guides.

IP 13/82. Conradson Carbon Residue of Petroleum Products.
IP 14/82. Ramsbottom Carbon Residue of Petroleum Products.
IP 19/76 (reapproved 1982). Demulsification Number Lubricating Oil.
IP 30/81. Doctor Test.
IP 91/76 (reapproved 1982). Bitumen Emulsion Residue on Sieving.
IP 102/74 (reapproved 1981). Fluxing Value of Flux Oil.
IP 146/80. Foaming Characteristics of Lubricating Oils.

IP 289/74 (reapproved 1981). Water Reaction of Aviation Fuels.

IP 312/74 (reapproved 1981). Frothing Characteristics of Emulsifiable Cutting Oil.

IP 317/75 (reapproved 1982). Residues in Liquefied Petroleum (LP) Gases.

Methods 13 and 14 are intended to provide an indication of coke-forming tendencies, and are in general applicable to non-volatile petroleum products which partially decompose on distillation at atmospheric pressure. The apparatus and operating conditions employed in the two tests are dissimilar, and no really satisfactory correlation has been found between the results of the two methods. Whilst at one stage there was indication that Conradson Carbon (IP 13) was to become obsolete, current opinion is that it is still needed, particularly for very viscous (bitumastic) products.

Method 19 is normally applied to turbine oil, but because it is sensitive to the ageing and contamination of the oil, it is unsuitable for the assessment of used oil and thus has a limited usefulness. Method 146 may provide similar information, but by a reverse procedure. Method 312 is used on cutting oils in the form of aqueous emulsions.

The Doctor Test (Method 30) is perhaps one of the oldest in use and is intended primarily for the detection of mercaptan sulphur compounds in volatile petroleum products. It is of more value to the refiner than the marketer, because modern refining methods generally completely eliminate the mercaptan sulphur which the test is designed to detect.

Method 289 is a valuable empirical test for indicating the ease and cleanliness with which water will separate from aviation turbine fuel.

CHEMICAL TEST METHODS

These are a little less numerous than the empirical test methods; in general they are based on well established analytical principles, and when adequately standardized, have satisfactory precisions. Nevertheless, it will be appreciated that in some of the groups described below, the same property is measured by procedures which in the interests of simplicity might well be combined.

Determinations of Acidity and Alkalinity

IP 1/74 (reapproved 1981). Acidity of Petroleum Products—Neutralization Value.

IP 37/66 (reapproved 1981). Acidity and Alkalinity of Greases.

IP 139/65 (reapproved 1981). Neutralization Number by Colour-indicator Titration.

IP 177/64 (reapproved 1979). Neutralization Number by Potentiometric Titration.

IP 182/82. Acidity (Inorganic) of Petroleum Products-Colour Indicator Titration Method.

IP 213/82. Acidity of Bitumen—Neutralization Value.

IP 273/78. Total Acidity in Aviation Turbine Fuel.

IP 276/75 (reapproved 1981). Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration.

IP 354/81. Total Acidity in Aviation Turbine Fuel.

Between them, they are applicable to all petroleum products. It would be nice to replace all the methods by a single procedure for the determination of neutralization value, with modifications for particular materials; however, an overall method would be very unwieldy, particularly when precision aspects have to be considered.

Methods 273 and 354 are different procedures for basically the same parameter. It is expected that Method 273 will be little used and eventually deleted.

Determinations of Ash, Sediment, and Water

IP 4/81. Ash from Petroleum Products.

IP 53/82. Determination of Sediment in Crude and Fuel Oils by Extraction.

IP 74/82. Water in Petroleum Products and Bituminous Materials by Distillation.

IP 75/82. Water and Sediment in Fuel Oils by Centrifuge.

IP 163/79. Sulphated Ash from Lubricating Oils and Additives.

IP 223/68 (reapproved 1978). Ash from Petroleum Products Containing Mineral Matter.

IP 291/73 (reapproved 1977). Water Content of Bitumen Emulsions.

IP 316/74 (reapproved 1982). Total Solids in Used Engine Oils.

IP 339/79. Total Metals in Unused Lubricating Oils and Additives—Complexometric Procedure.

IP 356/82. Water in North Sea Crude Oil by Karl Fischer Method.

IP 358/82. Determination of Water in Crude Oil by Distillation.

IP 359/82. Determination of Water and Sediment in Crude Oil by Centrifuge Method.

Except for Method 339 the above are straightforward analytical procedures which seemingly require little in the way of specialized techniques and apparatus, and could therefore be combined in certain cases. However, because of the fiscal situation with North Sea Crude and particularly water content, it was necessary to produce Method 356 specifically for North Sea Crude. At the same time Methods 358 and 359 were produced for crude oils generally, whilst the counterpart Methods 74 and 75 were limited for application to petroleum products and bituminous materials.

Extraction and Precipitation Procedures

It is frequently necessary to separate and estimate certain components from petroleum products or mixtures thereof, and for such purposes the following methods are available:

IP 47/82. Solubility of Bituminous Binders.

IP 105/82. Recovery of Bituminous Binders by Dichloromethane Extraction.

IP 137/82. Soluble Cutting Oil—Oil Content of Dispersions.

IP 143/82. Asphaltenes Precipitation with Normal Heptane.

IP 158/69 (reapproved 1979). Oil Content of Petroleum Waxes.

IP 162/76 (reapproved 1982). Soluble Binder Content of Bituminous Materials used in Roads and Buildings.

Of these, Method 143 is worthy of particular comment in that its use is specified in the UK Statutory Instrument, Customs and Excise, Hydrocarbon Oil Regulations 1973, where the term 'fuel oils' is stated to mean 'heavy oils which contain in solution an amount of hard asphalt of not less than one half of one per cent'.

Determination of Sulphur

Sulphur is to some extent the bugbear of the refining industry, except where it can be extracted and sold at a profit. One of the main criticisms is that it contributes to atmospheric pollution when fuels of appreciable sulphur content are burned. Also, sulphur and certain of its compounds, if present in petroleum products, can give rise to the corrosion of metal, notably steel and copper.

A knowledge of the sulphur content of petroleum products is therefore of importance to both refiner and user, and various methods have been evolved for its estimation in one form or another. Those listed below are in current use, and for completeness, although it is not strictly a chemical test, the latest Method 336 has been added. This is a physical analytical method and is applicable to a wide range of petroleum products, and it is quick, easy, and has good precision.

IP 61/65 (reapproved 1981). Sulphur in Petroleum Products by the Bomb Method.

IP 103/70 (reapproved 1978). Hydrogen Sulphide Content—Cadmium Sulphate Method.

IP 104/53. Mercaptan Sulphur Content—Silver Nitrate Method.

IP 107/73 (reapproved 1980). Sulphur in Petroleum Products (Lamp Method).

IP 155/77. Sulphur (Reactive to Copper) in Cutting Oils.

IP 242/69 (reapproved 1978). Sulphur in Petroleum Products—Flask Combustion Method.

IP 243/70 (reapproved 1978). Sulphur in Petroleum Products—Wickbold Oxy-hydrogen Method.

IP 272/71 (reapproved 1979). Mercaptan Sulphur and Hydrogen Sulphide Content of Liquefied Petroleum Gases—Electrometric Titration Method.

IP 336/81. Sulphur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence (Non-dispersive X-Ray Fluorescence).

IP 342/79. Mercaptan Sulphur in Gasoline, Kerosine, Aviation Turbine and Distillate Fuels (Potentiometric Method).

It should be noted that Method 104 is obsolescent. It is being temporarily retained until the following methods have gained wider recognition: IP 272 which replaces IP 104 (Method A), and IP 342 which replaces IP 104 (Method B).

Determination of Inorganic Constituents and Contaminants (Other than Sulphur)

The following methods are listed under this heading:

IP 110/82. Barium in Lubricating Oil.

IP 111/82. Calcium in Lubricating Oil.

IP 117/82. Zinc in Lubricating Oil.

IP 118/65 (reapproved 1981). Chlorine in New and Used Lubricants.

IP 149/80. Phosphorus in Lubricating Oils and Additives—Quinoline Phosphomolybdate Method.

IP 224/68 (reapproved 1978). Trace Amounts of Lead in Aviation Turbine Fuels and Light Petroleum Distillates.

IP 225/76 (reapproved 1982). Copper in Aviation Turbine Fuels and Light Petroleum Distillates.

IP 244/71 (reapproved 1979). Chlorine in Petroleum Products—Flask Combustion Method.

IP 245/81. Phosphorus in Petroleum Products—Flask Combustion Method.

IP 248/71 (reapproved 1979). Lead in Gasoline—Volumetric Chromate Method.

IP 270/77. Total Lead in Gasoline—Iodine Monochloride Method.

IP 271/70 (reapproved 1978). Barium in Lubricating Oil Additive Concentrates.

For certain reasons allied to deposit formation, catalyst poisoning, etc., it is desirable to eliminate any traces of lead or its compounds, particularly from turbine fuels and feed to catalytic reforming plants. Such traces are usually the result of contamination or of a refining treatment. Methods 224 and 225 cater for estimating trace lead and copper, respectively.

Lead compounds are added to gasoline to improve ignition quality; however, legislation has stipulated less lead in gasoline over the years. Consequently the determination of lead in gasoline has prompted development of quicker more accurate methods. Currently Method 270 is the best chemical method; however, physical analytical methods have been developed (see below) which will probably replace the chemical methods.

Modern lubricating oils contain additives based on a variety of elements, e.g. barium, calcium, chlorine, phosphorus, and zinc. As can be seen some of the above methods can be used for the estimation of these elements, although physical analytical methods are available which are proving to be more accurate and faster than the chemical procedures.

Determination of Organic Constituents by Chemical Means

The following methods are listed under this heading:

IP 84/81. Iodine Value—Iodine Monochloride Method.

IP 129/81. Bromine Number—Colour-indicator Method.

IP 130/78. Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration.

IP 136/72 (reapproved 1979). Saponification Number of Petroleum Products.

IP 144/81. Analysis of Oil Soluble Sodium Petroleum Sulphonates.

IP 284/72 (reapproved 1979). Saponifiable and Unsaponifiable Matter in Oils, Fats and Waxes.

IP 297/80. Furfuraldehyde in Petroleum Products.

IP 298/80. Quinizarin in Petroleum Products.

IP 299/78. Bromine Index of Petroleum Hydrocarbons by Electrometric Titration.

Four of the above methods, namely, 84, 129, 130, and 299, are generally intended to find a degree of unsaturation in the product. Methods 297 and 298 determine the quantities of Customs Markers, furfuraldehye and quinizarin in oils.

Again physical analytical methods are available which are more applicable to hydrocarbon types than some of the above.

PHYSICAL TEST METHODS

Although physical methods of assessment cover a wide range of properties, it is apparent that the advances made in recent years are in the realm of analysis rather than the determination of specific physical properties.

Physical Properties

The determination of these rests on the following procedures the majority of which are well established and in current use:

IP 59/82. Density and Relative Density.

IP 160/82. Density, Specific Gravity, or API Gravity of Crude Petroleum and Liquid Petroleum Products.

IP 189/82. Density Graduated Bicapillary Pyknometer Method.

IP 190/82. Density and Relative Density Capillary-Stoppered Pyknometer Method.

IP 235/82. Density and Relative Density of Light Hydrocarbons by Pressure Hydrometer.

IP 71/80. Kinematic Viscosity of Transparent and Opaque Liquids and the Calculation of Dynamic Viscosity.

IP 222/68 (reapproved 1982). Absolute Viscosity of Asphalts (Bitumen).

IP 226/80. Calculating Viscosity Index from Kinematic Viscosity at 40 and 100°C.

IP 267/82. Low Temperature Viscosity of Automotive Fluids Measured by Brookfield Viscometer.

IP 319/75. Kinematic Viscosity of Asphalts (Bitumen).

IP 171/65 (reapproved 1981). Vapour Pressure—Micro Method.

IP 12/79 (reapproved 1980). Heat of Combustion of Liquid Hydrocarbon Fuels.

IP 20/73 (reapproved 1980). Electric Strength of Transformer Oil.

IP 101/76 (reapproved 1982). Electric Strength of Bitumen.

IP 292/73 (reapproved 1980). Particle Charge of Bitumen Emulsions.

IP 295/73 (reapproved 1980). Electric Strength of Insulating Oils.

IP 55/77 (reapproved 1979). Melting Point of Petroleum Wax (cooling curve).

IP 17/52 (reapproved 1981). Colour by the Lovibond Tintometer.

IP 196/66 (reapproved 1981). ASTM Colour of Petroleum Products—ASTM Colour Scale.

IP 185/65 (reapproved 1979). Odour of Petroleum Wax.

IP 57/55 (reapproved 1981). Smoke Point.

IP 134/56 (reapproved 1979). Foreign Particles in Grease.

IP 216/71 (reapproved 1979). Particulate Contaminant in Aviation Turbine Fuels.

IP 275/71 (reapproved 1979). Microscopically Sizing and Counting Particles from Petroleum-Base Aerospace Hydraulic Fluids.

IP 274/82. Electrical Conductivity of Aviation Fuels Containing a Static Dissipator Additive.

IP 357/82. Permittivity of Bitumen.

The procedures for determining density, relative density, and specific gravity cover all types of petroleum products from gas to bitumen. Method 59 contains a Table which indicates the methods to use for a range of products under certain conditions. Method 160 is the general hydrometer method for most stable liquid petroleum products.

Of the remaining methods there is little to be said other than they all satisfy a particular need.

Physical Analytical Methods

Organic analysis

Perhaps the greatest advance in recent years is in chromatography, particularly gas chromatography, where several new methods are evident. A further technique, called high-performance liquid chromatography, is also proving useful, and further methods are being developed. Along with chromatography are other techniques such as nuclear magnetic resonance and refractive index. Perhaps a drawback in the use of these techniques is the cost of equipment which does not easily lend itself to routine laboratories. At the same time the advantage of speed and accuracy are greatly desired, plus the fact that they are generally adaptable to automation and in-line control.

Methods under this heading are:

IP 156/70 (reapproved 1978). Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption.

IP 214/66 (reapproved 1981). Analysis of Commercial Xylenes by Gas Chromatography.

IP 264/72 (reapproved 1979). Analysis of Liquefied Petroleum (LP) Gases and Propylene Concentrates by Gas Chromatography.

IP 282/77. Hydrocarbon Impurities in Commercial Benzene and Toluene by Gas Chromatography.

IP 296/73 (reapproved 1980). The Characterization of Pollutants of Petroleum Origin on Seas and Beaches by Gas Chromatography.

IP 318/75 (reapproved 1982). The Characterization of Pollutants of Petroleum Origin by High Resolution Gas Chromatography.

IP 337/78. Analysis of Non-Associated Natural Gas by Gas Chromatography.

IP 344/80. Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography.

IP 345/80. Analysis of Associated Natural Gas by Gas Chromatography.

IP 314/74 (reapproved 1981). Characterization of Oil and Tar Residues by Thin Layer Chromatography.

IP 343/80. 2,4-Dimethyl, 6-Tertiary Butyl Phenol in Aviation Turbine Fuels by High Performance Liquid Chromatography.

IP 277/72 (reapproved 1979). Icing Inhibitor in Aviation Turbine Fuels.

IP 338/82. Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry.

IP 346/80. Polycylic Aromatics in Petroleum Fractions by Dimethyl Sulphoxide—Refractive Index Method.

It should be noted that Method 277 has four methods depending on the type of finish: Method A uses infra-red spectroscopy, Method B gas chromatography, Method C an iodometric (chemical) finish, and Method D colorimetric.

Inorganic analysis

Physical analytical methods are replacing the long tedious wet-chemical methods for inorganic elements in petroleum products. The following are methods that come directly under this heading, although other procedures such as potentiometric, amperometric, and coulometric are used in titrimetric methods for petroleum analysis.

IP 122/62 (reapproved 1981). Spectrographic Analysis—Inorganic Constituents of Ashes.

IP 187/66 (reapproved 1981). Barium, Calcium, Phosphorus and Zinc in Lubricating Oils—Direct Reading Emission Spectrographic Method.

IP 228/72 (reapproved 1979). Lead in Gasoline by X-Ray Spectrometry.

IP 285/79. Vanadium and Nickel in Petroleum Products—Spectrophotometric Method.

IP 286/72 (reapproved 1979). Trace Amounts of Vanadium in Petroleum Products—Spectrophotometric Method.

IP 199/66 (reapproved 1981). Determination of Lithium and Sodium in Lubricating Greases by Means of a Flame Photometer.

IP 288/74 (reapproved 1981). Sodium, Nickel and Vanadium in Fuel Oils and Crude Oils by Atomic Absorption Spectroscopy.

IP 308/82. Barium, Calcium, Magnesium and Zinc in Unused Lubricating Oils by Atomic Absorption Spectroscopy.

IP 336/81. Sulphur in Petroleum Products by Energy-dispersive X-Ray Fluorescence (Non-dispersive X-Ray Fluorescence).

IP 352/81. Total Lead in Gasoline by Non-dispersive X-Ray Fluorescence Spectrometry.

IP 265/70 (reapproved 1978). Total Salts Content of Crude Oil—Conductivity Method.

RIG TESTS

The only sure way in which to ascertain the suitability of a petroleum product for its proposed use is to examine its actual performance over a prolonged period in the appropriate equipment, machine, or engine. This in most cases is impracticable and sometimes, impossible. A wide variety of rig tests have therefore been evolved with a view to obtaining performance data in a

reasonably short space of time. These concern engine fuels, kerosine, lubricating oil, and grease.

Engine Tests for Fuels

These, as will be seen in the list below, cover fuel from gas to diesel; they are well established and invariably find a place in the majority of engine-fuel specifications. As mentioned earlier, to avoid duplication the methods are contained in the *Annual Book of ASTM Standards,* Part 47.

IP 41/60. Ignition Quality of Diesel Fuels.
IP 119/60. Knock Rating—Supercharge Method.
IP 236/69. Test for Knock Characteristics of Motor and Aviation Type Fuels by the Motor Method.
IP 237/69. Test for Knock Characteristics of Motor Fuels by the Research Method.
IP 238/69. Test for Knock Characteristics of Liquefied Petroleum (LP) Gases by the Motor (LP) Method.
IP 325/82. Front End Octane Number (RON 100°C) of Motor Gasoline.

The equipment for these tests is expensive but the procedures have been meticulously standardized and the results are of acceptable precision. Although the knock rating methods are suitable and essential for the refinery control of fuel quality, it is maintained by many that they do not necessarily reflect road performance, and although much time and effort have been expended on attempts to devise a 'road knock test' no acceptable procedure of this type has yet been developed.

Attempts have been made to equate road performance with combinations of research and motor octane numbers. These equations can be satisfactory for a limited car population, but cannot be accepted on a general basis.

Method 325 measures the research octane number of the motor gasoline fraction of boiling range below 100°C. The result is generally lower in value than that of the whole motor gasoline. The method, covering the production of the fraction boiling below 100°C, is only described in the *IP Standards Book,* Part 1. The subsequent determination of the octane number is determined by method ID 237, as published in *ASTM Standards,* Part 47.

Rig Tests for Burning Oil

There are only two of these:

IP 10/65 (reapproved 1981). Burning Test—24-Hour.
IP 11/63 (reapproved 1975). Burning Test—Seven-Day.

As their titles indicate they provide a direct and practical assessment of burning qualities in wick-fed lamps. Although Method 11 is of very limited use, Method 10 is still of value in that it is the only means of assessing the char value of a burning oil when a very small quantity of a heavier oil such as lubricating oil is present. Even today's sophisticated methods for the detection of small quantities of one petroleum product in another do not as yet equal this test.

Engine Tests for Lubricants

The high stresses experienced in modern engines necessitate high-quality lubricants capable not only of withstanding extremes of pressure and temperature, but also of minimizing the effects of the decomposition of sulphur compounds and of the formation of oxidation products which contribute to the wear of bearings and to lacquer formation on piston, piston rings, etc.

Of the engine tests listed below designed to evaluate lubricant performance, two (Methods 176 and 246) employ a spark-ignition engine, and three (Methods 175, 231, and 279) employ compression-ignition engines.

IP 231/69 (reapproved 1978). Engine Cleanliness—Caterpillar High Speed Super Charged Compression-Ignition Test Engine.

IP 247/69 (reapproved 1978). Merit Rating System for Engine Cleanliness and Wear.

IP 175. Now CEC L-01-A-69 (see Note). Engine Cleanliness—Petter AVI Compression-Ignition Test Engine.

IP 176. Now CEC L-02-A-69 (see Note). Oil Oxidation and Bearing Corrosion—Petter W1 Spark-Ignition Test Engine.

IP 246. Now CEC L-03-A-70 (see Note). Ford Cortina High Temperature Test.

IP 279. Now CEC L-13-T-74 (see Note). Engine Cleanliness—Petter AVB Supercharged Compression-Ignition Test Engine.

Note. Methods 175, 176, 246, and 279 are no longer IP Methods. They have been adopted as CEC Standard Methods of Test.

Like the methods of knock-rating, the above methods have been carefully standardized and incorporated in specifications for lubricating oils. It is to be noted that the anti-wear, anti-corrosive, dispersancy, etc. qualities of present-day lubricants are largely conferred by additives, many of which are organometallic compounds, the detection and measurement of which have been touched upon in the foregoing. Method 247 is not an engine test method, but provides a systematic method of assessing the results of engine tests.

Rig Tests for Lubricants

As for engines, the stresses to which present-day gears and transmissions are subjected are considerably greater than heretofore, and lubricants for such mechanisms must be capable of withstanding the high pressures involved. Thus it is desirable to have means whereby the suitability of lubricants for gears and transmissions can be gauged. The following methods are in many cases specific for this purpose, whilst in some cases they are more general.

IP 166/77. Load-Carrying Capacity Test for Oils—IAE Gear Machine.

IP 232/69 (reapproved 1979). IP High Torque Test Procedures for Hypoid Oils at 225°F (107.2°C) and 275°F (135°C).

IP 233/69 (reapproved 1977). IP/MIRA High Speed Endurance Test Procedure for Hypoid Oils in Passenger Cars.

IP 234/69 (reapproved 1977). IP/MIRA High Speed Shock Test Procedure for Hypoid Oils/Axles in Passenger Cars with Non-automatic Transmission.

IP 239/82. Extreme Pressure Properties: Friction and Wear Tests for Lubricants: Four Ball Machine.

IP 240/82. Extreme Pressure Properties, Friction and Wear for Lubricating Fluids: Timken Wear and Lubricant Testing Machine.

IP 241/73 (reapproved 1977). Extreme Pressure Properties, Anti-wear, Friction and Corrosion Protection Properties of Fluid Lubricants: Falex Machine.

IP 281/80. Anti-Wear Properties of Hydraulic Fluids—Vane Pump Test.

IP 294/79. Shear Stability of Polymer-containing Oils Using a Diesel Injector Rig.

IP 300/82. Rolling Contact Fatigue Tests for Fluids in a Modified Four-Ball Machine.

IP 305/79. The Assessment of Lubricants by Measurement of their Effect on the Rolling Fatigue Resistance of Bearing Steel Using the Unisteel Machine.

IP 313/77. Air Release Value.

IP 332/77. The Coefficient of Friction of Automatic Transmission Fluids—DKA Friction Machine.

IP 333/77. Measurement of the Anti-Wear Properties of Automotive Brake and Clutch Fluids by a Stroking Test.

IP 334/80. Load Carrying Capacity Test for Oils—FZG Gear Machine.

IP 350/81. Standard Test Method for Apparent Viscosity of Engine Oils at Low Temperature Using the Cold-Cranking Simulator.

IP 351/81. Shear Stability of Polymer-Containing Oils Using the FZG Gear Rig.

There has been a considerable increase in the number of rig test methods, the majority of them being very specific. Unfortunately lubricants and their end-uses do require this specificity in testing.

Rig Tests for Greases

For lubricants in a liquid state, rig tests are applied to greases to evaluate such characteristics as resistance to extreme pressure, low temperature, water, and rusting. These methods are as follows:

IP 168/79. Rolling Bearing Performance Test for Lubricating Greases.

IP 186/78. Low Temperature Torque Test—Lubricating Greases.

IP 215/66 (reapproved 1981). Water Washout Characteristics of Lubricating Greases.

IP 220/81. IP Dynamic Anti-rust Test—Lubricating Greases.

IP 326/80. Extreme Pressure Properties, Friction and Wear for Greases—Timken Wear and Lubricant Testing Machine.

It must also be noted that Method 239, the Four-Ball Machine, can also be used for greases.

IN-LINE TESTING

Since the 1950s process analysers have been developed and applied to measure continuously the quality of material within or drawn directly from the flowing

line. The benefits are very considerable in terms of reducing sampling and testing time, improved precision, increased number of tests on each batch of product, the opportunity for automatic control of quality, and reduction in testing effort.

Analysers are commonly used for the following key properties of the principal types of petroleum products:

Gases: Composition, sulphur compounds, moisture.
Gasoline: R.V.P., distillation, octane rating.
Middle Distillates: Flash point, distillation, cloud/pour point, sulphur.
Heavy oils: Viscosity, sulphur.
All products: Density.

To date one general method and five specific methods appear in the 1982 *IP Standards* as follows:

IP 340/82. IP Code of Practice for Calibrating and Checking Process Analysers—A General Guide to the Principles and Methods used.
IP 341/82. IP Code of Practice for Calibrating and Checking Process Analysers—Capillary-type Viscosity Analysers.
IP 347/82. IP Code of Practice for Calibrating and Checking Process Analysers—Cloud Point Analysers.
IP 348/82. IP Code of Practice for Calibrating and Checking Process Analysers—Distillation Analysers.
IP 349/82. IP Code of Practice for Calibrating and Checking Process Analysers—Flash Point Analysers.
IP 353/82. IP Code of Practice for Calibrating and Checking Process Analysers—Gas Chromatography Analysers.

The effort in producing the above has been considerable and the methods are of great importance to the industry, initially on the production side, and also in other areas such as marketing plants, particularly since transportation of many petroleum products is by pipeline.

SPECIFICATIONS

Specifications for petroleum products may be 'official' such as those published by the British Standards Institution,[2] they may be agreed between vendor and purchaser, or they may be advised jointly by the marketer and the refiner as representing current market requirements. Refiners may have manufacturing specifications that are somewhat stricter than the market specifications in order to allow for the possible deleterious effects of storage and transport on their products.

Currently, in order to conserve oil and make the most from the crude, specifications have tightened-up so that there is little if any slack in the system. For example, there are now only three grades of petrol sold in the UK, the highest octane fuel having been taken off the market. This meant, certainly for a period, that some high compression ratio cars did not have the correct grade available. Also the improvement in precision and automation of test methods, particularly process analysers, has enabled the refiners to control the limits of specifications more easily.

The ideal specification is one which gives complete control of product quality without being over-restrictive, contains the minimum requirements to satisfy quality demands and moreover incorporates the minimum number of established meaningful test methods.

Although performance tests are the ultimate criteria of quality, they are too costly, time-consuming, and imprecise for use as quality control tests, and so other properties must be found which can be established simply and precisely by laboratory tests, and which correlate with performance.

Unfortunately, as the industry has grown tests have been added to specifications so that in many cases an overlap of tests measuring similar properties has occurred; for example, a turbo-jet fuel specification can contain smoke point, aromatic content, aniline point, luminometer number, hydrogen, and density, all of which can in some way be interrelated.

What is essential to specifications is the statistics of the test methods, i.e. the repeatability and reproducibility of the test. First, because the reproducibility should be considered when setting the limit, particularly to set a limit such that a test on the product by another laboratory will not give a result outside the limit of the specification, and secondly where a limit has been agreed for the specification of a product, then to know what the customer should accept on testing of the product on receipt. This type of statistics is covered in a British Standard.[3]

The assessment of quality is an area where improvement is always being sought. The emphasis towards quicker, more precise, and automatic test methods is ever the goal, and the last decade has seen a big improvement in this area. Perhaps the specification writers need to accept some of these new tests methods more readily, or having accepted them to weed out redundant methods that the new ones were designed to replace.

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2. (i) Petroleum Fuels for Oil Engines and Burners, BS 2869. (ii) Petrol for Motor Vehicles, BS 4040.
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The Classification of Petroleum for Safety Purposes and its Use in Codes of Safe Practice

By P. JONES

The design, layout, construction, and operation of a petroleum facility, whether it is a refinery (see Chapter 10) or a distribution and storage installation as covered in Chapter 33, are based upon a classification system of the various volatility categories according to the flammability hazard defined by flash point level (see below). Such a classification is then used as a basis for design, layout, and operating procedure, graded carefully for each category, enabling accepted code standards to be promulgated. An example in the UK is the Institute of Petroleum's series of Model Codes of Safe Practice. In the USA comparable codes are produced by the American Petroleum Institute (API), and such is the case in other countries.

THE IP CLASSIFICATION

Since the 1973 edition of this volume, the Institute of Petroleum has revised its classification for petroleum and its streams to be consistent with the system that is adopted within the EEC in its directives for the classification of flammable hazardous substances. UK legislation is likewise in the course of adapting to the EEC procedure.

The IP classification is based, except for flammable gases and liquefied petroleum gases (LPG) which are a separate category, on closed-cup flash points as shown in the table below.

In this system high vapour pressure material such as gasoline or crude oil is a 'Class I' petroleum, kerosine (flash point typically about 38°C) falls into

IP classification	Range of limits	Corresponding UK and EEC legal terminology
Class O	Liquefied Petroleum Gas (LPG)	Liquefied Petroleum Gas
Class I	Liquids which have a flash point below 21°C.	Highly flammable liquid*
Class II	Liquids which have a flash point from 21°C up to and including 55°C.	Flammable liquid
Class III	Liquids which have a flash point above 55°C up to and including 100°C.	Combustible
Unclassified	Liquids which have a flash point above 100°C.	(No designation, but will burn under appropriate conditions—see later)

* That is, replacing the UK earlier definition 'petroleum spirit' under the 1928 Act (see later footnote).

'Class II', while diesel (DERV) and gas oils, both with a flash point greater than 55 °C, are 'Class III'. Fuel oils will also be 'Class III', or if the flash point is in excess of 100 °C, 'Unclassified'.

EFFECT OF TEMPERATURE

The flash point of a flammable material is an indication of the temperature above which it will evolve sufficient vapour for it to be ignitable by a source of ignition in the presence of air. Below the temperature corresponding to the flash point it will not burn, except in the case where the liquid is present as a mist, spray, foam, or film, which can be ignited even at temperatures well below the flash point (see later).

Subdivision of the Classification for High Ambient Temperatures and for Heated Products

For countries where ambient temperatures are high enough for the normal handling of products to rise above 21 °C, e.g. in tankage, or in circumstances where products are handled artificially heated, it is necessary to introduce a further subdivision of the classification. For example, kerosine with a flash point, say, of 38 °C, would be classified as 'Class II' petroleum for ambient handling in a temperate climate, since its vapour would be too lean to create a flammable atmosphere; handled in a tropical country its temperature could rise to above the level of its flash point, creating a potential flammable condition (e.g. in the vapour space of a fixed-roof storage tank).

For this reason, in the IP Codes Class II and Class III categories of petroleum are further subdivided in accordance with the circumstances as follows:

Sub-division of Class II and III liquids

Class II (1)	Liquids which have flash points from 21 °C up to and including 55 °C, handled below flash point.
Class II (2)	Liquids which have flash points from 21 °C up to and including 55 °C, handled at or above flash point.
Class III (1)	Liquids which have flash points above 55 °C up to an including 100 °C, handled below flash point.
Class III (2)	Liquids which have flash points above 55 °C up to and including 100 °C, handled at or above flash point.

Reference has been made to current UK legislation following the 21 °C, 55 °C, and less importantly the 100 °C flash point limits. In this change, the former definition 'petroleum spirit' (with its narrower connotation) under the earlier Petroleum (Consolidation) Act 1928, as a substance having a closed flash point below 73 °F (22.7 °C), is being subsumed into the broader categories given—that of 'highly flammable liquid' for any such liquid flashing below 21 °C, and 'flammable liquid' for any flashing between 21 °C and 55 °C. Such a broadened definition applies equally to materials whether of petroleum, chemical, or natural origin.

Also still on the statute book under the Factories Act 1961 Regulations, is the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972, for storages on factory premises. These are required to have signs such as 'Highly Flammable. Flash point below 32 °C', and apply to materials in the range of flash point between 22.7 and 32 °C not covered by the earlier 1928 Act, and for LPG 'Highly Flammable—LPG', respectively.

This subdivision is used as follows in conjunction with the IP Codes of Safe Practice.

Where liquids to be handled are in the category Class II (1) or Class III (1), i.e. at temperatures below their flash point, appropriately less stringent conditions of safety spacing and related precautions are given in the codes than are applicable for Class I products (i.e. highly flammable liquids).

When Class II or III products fall into the Class II (2) or III (2) category, they are treated as though they were in Class I.

This system of classification enables requisite guidance to be given, and readily understood and followed in the codes, both for design and subsequent operation.

Since any combustible liquid represents a fire hazard at temperatures above its flash point, 'Unclassified' petroleum liquids should be considered as Class III (2) when handled under this condition.

Principles of Flammability and the Prevention of Fire and Explosion

Even small quantities of petroleum vapour in air can form a flammable mixture which can be ignited by a flame, hot element, spark, or other source of ignition. On its own a flammable gas or liquid cannot ignite or explode, e.g. when contained in a wholly enclosed vessel, pipeline, or container. For there to be the possibility of ignition or explosion two other factors must be present, namely: (1) the presence of air or oxygen in appropriate proportions to support ignition, and (2) an ignition source of sufficient intensity. These three factors are sometimes called the 'fire triangle'; with any one of these three missing, fire or explosion cannot occur.

In the case of a liquid it is important to recognize that the *liquid* itself does not burn; it is the vapour given off by the liquid that burns. Low flash point products such as gasoline have a sufficiently high vapour pressure to give off vapour at temperatures as low as $-45\,^{\circ}C$; high flash point low vapour pressure materials like diesel or fuel oil, with flash points in excess of $55\,^{\circ}C$, have to be heated to give off vapour sufficient to burn.

For petroleum vapours or gases to form a flammable mixture in air the concentration of that substance in air must lie within the 'flammable' or 'explosive' range.

For petroleum products generally the 'flammable' or 'explosive' range (the two terms are used synonymously) lies between the range of about 1 per cent to 8 per cent by volume in air. When the concentration of vapour is under 1 per cent the mixture is said to be too lean to burn, or below the 'lower flammable limit'; when the concentration of vapour is over 8 per cent, the mixture again will not burn, and is said to be 'too rich' or above the upper flammable limit.

A table of flammable limits in air for some gases and liquids encountered in petroleum processing is given in Appendix 4 of the IP Refining Code. Hydrocarbon light gases have somewhat wider limits (e.g. methane 5 vol % - 15 vol %), while the special case of hydrogen, flammable between the very wide range of 4 per cent and 75 per cent in air, should be noted.*

* It should be noted there is no essential difference between 'gas' and 'vapour'; the latter term is used in respect of a substance, e.g. gasoline, which is usually handled as a liquid.

Oil Present in the Form of Mist, Spray, or Foam

There is an additional factor to the above that is important in the handling of petroleum. It is that an oil may burn even though its temperature is below the flash point if it is in the form of a spray, mist, or foam.

Thus, although a low vapour pressure product, such as a kerosine, gas oil, lubricating oil, or fuel oil at the temperatures at which they are normally handled, gives rise to a vapour concentration in the tank or vessel in which it is contained which is normally 'too lean' to burn, the atmosphere in the vapour space with such products may be ignited at temperatures below their flash points if the product is present in the form of a mist, spray, or foam, such as may be caused by rapid or turbulent filling, jetting, or agitation of the liquid. The reason is that a source of ignition may vaporize the mist or spray droplets in its immediate vicinity and ignites that vapour, from which the flame propagates by the successive vaporization and burning of droplets throughout the mass of mist or spray. As an example, a kerosine mist can be ignited at a temperature of below 0°F (−17.8°C), whereas to produce sufficient vapour to reach a flammable concentration, the kerosine would have to be heated to about 100°F (38°C), its flash point.

The heat produced above the liquid surface by droplet combustion may so increase the rate of vaporization of the liquid as to bring in turn its vapour within the flammable range.

Since the formation of mist or spray can also create the hazardous generation of electrostatic charge build-up, it is necessary that precautions are taken during operation so that mist and vapour do not occur. (See later—Static Electricity.)

Akin to the flammability of a substance in the subdivided droplet form, is the situation where a thin film of oil spilled upon the ground, or a soaked cloth, will also ignite with a source of ignition, the so-called 'wicking effect'.

Facility Layout for Safe Spacing

The importance of ensuring that flammable concentrations of vapour do not occur in circumstances where there is the possibility of their ignition may be seen from the fact that five litres of gasoline are capable of producing over 2000 cubic feet of a flammable air/gas mixture. Areas in which a flammable atmosphere may arise are therefore carefully controlled, both by the provision of adequate safety distances set in the codes according to the flash point classification, and by control over all potential sources of ignition in such areas.

In this respect and where there is a possible discharge or the presence of flammable gas, vapour, or liquid, the consideration of safety distances is that of the ability to disperse such releases safely to below the lower flammability limit before they are able to reach adjacent facilities or a public boundary where a source of ignition or the possibility thereof could be encountered.

While there are a number of theoretical approaches for the calculation of dispersion, the subject is complex and is dependent upon the assumption that the released quantity will be known, while there are meteorological uncertainties. However, in the petroleum industry there is an extensive amount of experience of actual operational circumstances from which it is possible to

assess realistic distances which have stood the test of time in affording safety, and thus 'codes of experience' have become of high reliability. The following section outlines the procedures for the classification of areas for the selection and installation of electrical equipment.

Area Classification of Petroleum Installations for the Selection of Electrical Equipment

Unprotected electrical equipment would be a potential ignition hazard in certain areas of the installation. For the selection of appropriate and safe electrical equipment, and its siting in any oil facility, control is exercised by means of 'Area Classification', a procedure whereby the different zones of an installation or plant are set out in accordance with the International Electrotechnical Commission nomenclature, I.E.C. 79–10 (1972).

The definition of 'hazardous area' in this context, and its converse, is as follows:

Hazardous area

An area in which explosive/flammable gas-air mixtures are, or may be expected to be, present in quantities such as to require special precautions for the construction and use of electrical apparatus.

Non-hazardous area

An area in which explosive/flammable gas–air mixtures are not expected to be present in quantities such as to require special precautions for the construction and use of electrical apparatus.

Classification of Hazardous Areas

A Hazardous Area is divided into *zones* for the assessment of electrical equipment as follows:

Zone 0 In which an explosive/flammable gas–air mixture is continuously present for long periods.

The vapour space of a closed process vessel or storage tank or above an oil–water separator basin is an example of this zone.

Zone 1 In which an explosive/flammable gas–air mixture is likely to occur in normal operation.

The vicinity surrounding vents and gauging openings on a fixed-roof tank containing Class I petroleum is an example of this category.

Zone 2 In which an explosive/flammable gas–air mixture is not likely to occur and if one occurs it will only exist for a short time.

An example is the whole area inside the bund wall of a fixed or floating-roof tank containing Class I petroleum, and to the height of the bund wall.

Because of the lower probability of a Zone 2 occurrence, less stringent protection will be required for electrical equipment suitable for Zone 2 installation.

In the above classification the words 'explosive' and 'flammable' have, as stated before, the same meaning.

From the preceding discussion of the classification of petroleum it will be seen that hazardous areas may develop where Classes I, II (2), or III (2) products are handled or stored (or where the oil may be present in the form of spray, mist, or foam).

Detailed reading and examples on this important subject will be found in the IP Electrical, Marketing, and Refining Codes, and in the 'European Model Code of Safe Practice in the Storage and Handling of Petroleum Products: Part II Design, Layout and Construction, 1980' (obtainable from the Institute of Petroleum); BS 5345, Parts 1 and 2, BS 5501, Parts 1 to 7 and BS 4483, Part 2 describe the different categories of protected electrical equipment appropriate to each zone.

Non-electrical Sources of Ignition

'Area Classification' as described relates to the selection of appropriate electrical apparatus for use (or its exclusion) in the various zonings of a plant according to the degree of hazard, and precautions will be necessary also for other sources of ignition. In some cases, e.g. the adoption and protection of diesel-operated equipment, the procedures, as described later, may follow closely those of area classification. In other cases, e.g. the location of fired heaters, other experience criteria will be used.

Precautions against General Ignition Risk: Work Permit System

In areas classified as Zone 0 and Zone 1 all items of equipment should be considered very carefully, and if they could form an ignition source should be omitted. In Zone 2 areas no plant, equipment, or facilities should be used giving rise to fire, capable of producing sparks or generating temperatures higher than the auto-ignition temperature of the material gas–air mixture present (see, however, 'Work Permits' below for controlled work).

General precautions against all ignition means are applied, even outside of area classification zones, by declaring a larger area of an oil refinery or storage installation a 'Restricted Area'. This is an area in which management exercises control over all movements and operations, e.g. the area within the boundaries of all depots, installations, process areas, and jetties. Special safe areas, e.g. workshop areas, may also be designated where work involving welding, brazing, etc. (or smoking) may be carried out.

Within 'restricted areas', vehicular access will be controlled, and smoking and the carrying of matches, etc. prohibited, and all work which could involve a risk is subject to control by 'work permit'. Work permits describe the precautions (e.g. isolating, emptying, and gas-freeing, etc.) which may be required, and the conditions under which work can be carried out. Where 'hot-work' is required, gas testing certificates are required to be issued to ensure that a hazardous atmosphere is not present (see later). Other permits cover, *inter alia*, the safety of excavation work, isolation of electrical systems before maintenance, use of radioactive inspection equipment, testing for the absence of a toxic or oxygen-deficient atmosphere.

An outline of some of the principal measures for control of non-electrical ignition hazards is given below.

Static Electricity

Petroleum liquids such as distillates (or 'white oils') have low electrical conductivity and are known as 'static accumulators', because charges built up by the passage of such products through pipelines, filters, by splash filling of tanks or tanker vehicles, or by settling out of water droplets, mist particles, or the passage of a stream of air through the liquid can build up to dangerous levels. The charges on these liquids dissipate only over a period of time, called the relaxation time (see below). Residues or crude oil which contain asphaltenes ('black oils'), on the other hand, have much higher conductivity and are known as 'static dissipators', since charges generated disperse rapidly and do not build up to levels that can cause a hazardous spark.

Earthing

The best known method of combating the accumulation of electrostatic charge on a conducting body, such as a tank shell, piping, or a tank car, is to earth it. Earthing is described in the IP Electrical Code: whereas good earthing is essential, it will not eliminate the accumulation of electrostatic charges in an oil of low conductivity, since such charges cannot leak away quickly to the earthed tank wall. Consequently the entering liquid may cause accumulation of charge, ultimately producing, if the flow velocity is too great, a spark discharge from the liquid surface to nearby earthed bodies. Insulated conductors adjacent to such charged liquids may also acquire very high potentials, with the risk of electrical discharge, so that all conducting objects within a tank such as floating roofs and covers, gauge floats, etc. should be electrically bonded to the tank shell. Tank cars handling low-conductivity oils should be earthed before being loaded or unloaded, and bonded to the earthed product lines and loading arm prior to and during the transfer operation.

In regard to the 'static accumulators', the generation of a static electrical charge in itself does not present a hazard, e.g. in an enclosed vessel or pipeline; it is a hazard only when in the presence of a flammable atmosphere which could be ignited by the discharge of a spark. As charge generation is approximately proportional to the square of the linear velocity of the liquid flow, and will be considerably increased by the presence of relatively small quantities of free water, or any other separate dispersed phase, droplets or particles, precautions are taken to avoid the splash filling of tankage or tanker vehicles which could cause the formation of mist, foam, or spray, and the linear velocity in the inlet line or loading arm is customarily limited not to exceed 1 m/s until the filling outlet is completely submerged. If free water is present, or may be present, this rate should be maintained throughout the whole transfer. In the case of the filling of a storage tank a residence time of at least thirty minutes should be allowed after pumping has stopped before manually dipping or sampling which would involve introducing a conductive item such as a metallic sampling can into the tank vapour space. Where the product can be assumed not to contain free water, in loading into smaller vessels such as a road or rail tank car,

and there are no micro-filters, the residence time from completion of filling to manual dipping or sampling can be reduced to a minimum of two minutes.

Static Dissipative or Conducting Products

The above precautions are not necessary for 'black oils' which have a high conductivity, for the reasons stated. It is also possible to add an anti-static substance to a low conductive white oil product, which will have the same effect, and this is often used, e.g. with aviation fuels.

Static from Jets

Static electricity can be generated by a jet of gas, compressed air or steam when the stream contains liquid or solid particles, with the formation of a charged mist. The nozzle of such a jet should be earthed and bonded to the tank. If there is a possibility of a flammable atmosphere being present it is recommended that cleaning by steam jet should be avoided in vessels or tanks above a certain size.

In the case of a jet of water, with its high conductivity, any charge generated at the nozzle will leak back through the water jet itself to the earthed nozzle if the jet is unbroken. If it breaks into droplets after leaving the nozzle then such a charge can be retained in the spray or mist. In tank cleaning charge can also be generated when the jet impinges against the shell. Therefore tank cleaning with high-pressure water jets should be carried out after gas-freeing or inerting.

Tank cleaning with a jet of hydrocarbon oil can also result in charge generation on the spray or mist, and as in marine service, should be carried out only after inerting.

Clothing

An electrostatic charge may be built up by friction between clothing and an external surface, or by the removal of a garment, particularly one of synthetic material. This body charge may build up to such a value that an incendive spark may discharge to an earthed conductor. To avoid such an occurrence in the presence of a potentially flammable atmosphere, conductive (anti-static) footwear should be worn.

Fuller guidance on static electricity will be found in the IP Marketing and Refining Codes, and in BS 5958, Parts 1 and 2.

Auto-ignition—High Surface Temperatures

Care should be taken to distinguish between flashpoint, which is the temperature at which a product will give off sufficient vapour to be ignited by a flame, spark, or other ignition source, and the Spontaneous Ignition (or auto-ignition) Temperature (SIT). The latter is the temperature at which the substance will self-ignite in the presence of air without the application of any source of ignition.

Most petroleum products have SITs between 250°C and 500°C, and oil which has soaked into insulation can ignite at a temperature below its SIT. High-temperature surfaces above these levels, such as HP steam lines, furnace

outlet lines, etc., should be protected from coming into contact with oil, and the soaking of insulation by oil avoided by means of cladding and good preventive housekeeping.

Engines/Driving Units

No gasoline engine should be employed in an oil installation anywhere but in a non-hazardous area.

Diesel engines for powering certain items of equipment are commonly used in various areas of an installation, e.g. for pump sets or temporary maintenance. Flames or hot particles from an unprotected exhaust can be a source of ignition, and when operated in an area in which there is any risk of flammable vapour the 'Recommendations for the Protection of Diesel Engines Operating in Hazardous Areas', published by the Oil Companies Materials Association, London, should be followed.

Pyrophoric Deposits

Iron sulphur compounds may deposit on the walls of a vessel, pipeline, or storage tank by the reaction of iron with hydrogen sulphide or other sulphur compounds present in sour crudes or distillates. When exposed to the ingress of air, e.g. on opening a vessel or pipeline, this material may oxidize rapidly and reach a glowing temperature at which any flammable hydrocarbons present will ignite. Precautions are to exclude air and cooling such deposits, e.g. by wetting with water during the opening up of the equipment, keeping it wet while it is being worked upon.

'Hot-work'

Hot-work, which includes electric and gas welding and cutting, blow lamps, stoves, tar kettles, use of unprotected lighting, grit and shot blasting, power-operated grinders and cutting machines and other power-operated metallic tools, hand-operated tools in contact with dry concrete, stone or masonry, etc., is a particular activity for meticulous control, since in the course of repair and maintenance it is frequently necessary for such work to be carried out on or in plant and vessels which have contained flammable contents, and/or in areas where a source of these may be present.

The Work Permit system previously outlined is used to control each step to ensure that such work is safe. This will include, for tanks, vessels and pipework, their emptying, depressurizing, isolating of all lines and connections (by positive means such as spading or blanking off, since valves alone are not adequate), gas-freeing, etc., and then the issue of a gas-free certificate to indicate that it is safe for personnel to enter the vessel and/or to carry out the prescribed hot-work.

Full details of the Work Permit system for both 'hot' and 'cold work' are given in the IP Marketing and Refining Codes, and in their appendices also the measures that are necessary to ensure that gas detector instruments are checked and used reliably.

It is important to note that a gas detector instrument will register the

presence of gas or vapour only in the flammable range. It will not indicate the presence in equipment of combustible material such as kerosine, gas oil, or heavy oil. Thus it is important when authorizing hot-work to ensure that no such material remains, since application of heat may vaporize oil lying in rust, scale, seams, or as surface films to produce flammable vapour.

Tools—Impact Friction, etc.

It is a misconception that so-called safety alloy or 'non-sparking' tools are any safer than conventional steel tools. It has been established that both ferrous and non-ferrous tools can generate incendive sparks with concrete or stone. Smears of light alloy material such as aluminium on steel tools can increase the risk of ignition, especially if the tools are rusty. Where mechanical work is in progress the surrounding area should be free from flammable gases, and where appropriate the work should be kept well wetted with water.

The use of these tools is classified as hot-work, for which a work permit is necessary, as indicated above.

Summing up, in either a refinery or other oil installation where maintenance and repair work is to be carried out, it is essential that all concerned, whether installation or contractor personnel, are in no doubt as to the methods to be employed and the precautions to be taken to make the job safe. Non-electrical sources of ignition must be sited in safe areas. Where naked lights or hot-work of any form are necessary, a Work Permit system should be employed. These permits should be issued for a limited period and should stipulate specific work procedures.

Stray Currents

It is possible for stray electrical currents to be present unintentionally. Where railcar sidings are connected with main-line electrified tracks, they should be fully insulated. Care must be taken to ensure that rolling stock is not left in such a position as to bridge the insulated portion. The sidings should be earthed as an added precaution.

Where electric welding machines are used, cables should be in good condition and should be carried across pipelines on insulated bridging. Earths should be connected direct to the machine, and positioned no more than a few feet from the job. The use of installed equipment for earth routeing should be prohibited.

Fire Extinction

The same principles concerning flammability and combustion that were described earlier in this chapter are also relevant in relation to the extinction of fire, or the prevention of its spreading, since these are dependent upon: (i) removing or shutting off the source of the combustible material or excluding air, so that the mixture of vapour and air is no longer within the flammable limits, or (ii) cooling the body of the combustible material, together with structures, vessels, and equipment exposed to the conflagration to below the temperature at which combustion can continue.

The employment of an adequate water supply for such purposes, using fixed or mobile monitors to direct cooling water as a protective curtain, has been mentioned in other chapters, and also the provision of adequate foam-making materials for blanketing a fire.

Although a fire should normally be extinguished as rapidly as possible, e.g. as on a tank, it must be remembered that if this is done before all the fuel feeding it has been exhausted, or cut off, then it may re-ignite with worse consequences. This is particularly the case for a vapour or very volatile liquid leak which has ignited (e.g. LPG), since to extinguish such a leak without cutting off its supply is to risk a continued dispersion of flammable vapours over an increasing area which may reach a more remote source of ignition and ignite with explosive consequences.

Details of fire-fighting provisions are given in the IP Marketing and Refining Codes, and in the Fire Training Manual of the UK Petroleum Industry Training Board and API Publication 2021.

Marine Terminals

For a marine terminal, berth, or jetty where flammable petroleum cargoes are loaded or unloaded, guidance may be obtained both from the IP Refining and Marketing Codes, the 'European Model Code of Safe Practice in the Storage and Handling of Petroleum Products: Part II, Design Layout and Construction, 1980', and additionally from the 'International Safety Guide for Oil Tankers and Terminals (ISGOTT)', published on behalf of the International Chamber of Shipping/Oil Companies International Marine Forum (OCIMF) by Witherby and Co., London, from whom a brochure of related marine practice guides can be obtained.

CONCLUSION

An outline only can be given in this short chapter of some of the basic safety principles involved in the layout, operation, and maintenance of an oil installation. The details should be obtained from the codes mentioned in the text.

The subjects of LPG installations and Bitumen plants are outside the scope of this chapter, but are covered in detail in the IP Model Code of Safe Practice in the Petroleum Industry, Part 9, Liquefied Petroleum Gas Safety Code, and Part 11, Bitumen Safety Code.

Recommended further reading: J. R. Hughes. *Storage and Handling of Petroleum Liquids*. Charles Griffin and Co. Ltd., London.

33

The Petroleum Installation

By P. JONES

THE petroleum installation is important in the distribution of petroleum products in that it forms the intermediate holding point between the refinery and the customer.

To understand the necessity for such links in the chain of supply it may be helpful to analyse the market breakdown of one major UK oil company into the four broad categories of consumers as follows: (1) retail, covering sales of automotive products through garages and service stations; (2) industrial and commercial, covering large contracts for bulk supply of products, notably fuel oils for electricity generation and industrial heating, contract supplies of auto-diesel to transport companies, and gas oil for commercial heating purposes; (3) authorized distributors, covering small volume sales of kerosines and gas oil to smaller industrial and commercial customers and to agriculture, and paraffin and domestic heating oil to households; (4) special products.

The breakdown (UK Price Commission Study) is shown in Table I.

Of the four categories listed, industrial and commercial sales supplied direct by the company are the largest, amounting to about 65 per cent of total sales volume, although with considerable variation ranging up to the very large volumes of fuels for electricity production (this now is a decreasing usage).

The petrol retail (service station) sector is the next in volume (22 per cent); for the company concerned there were some 5500 such outlets, some owned and operated, and some supplied by agency agreements. Supply to all of these obviously requires a complex network chain.*

The diversity of the consumption pattern increases further when the low-volume customers in the domestic heating and the agricultural, small business and paraffin markets are taken into account, which together amount to a total of only 8 per cent of company sales, although each may comprise some 100 000 customers. For the major company to supply such low-volume markets directly, e.g. with typical deliveries of probably no more than 5000 litres would be to incur high unit costs; such trade is normally allocated to independent small suppliers known as 'authorized' or 'marketing distributors', each receiving and handling through its own facilities the bulk supply from the major company. An oil company may well have of the order of fifty or more authorized distributors, each operating from an approximately similar number of plants.

The extent to which such a complex of market outlets could be catered for by supply direct from the refinery to the ultimate consumer will be seen to be limited, either to fairly large consignment volumes (e.g. the block train or in some instances pipeline) and/or by the local radius of supply for other

* The UK retail sector as a whole comprised some 24 108 outlets at the end of 1982, according to the annual Institute of Petroleum survey, published in *Petroleum Review*, March 1983; the number of company-owned outlets was 7563; there were also 8000 outlets retailing derv, 2380 of these being company-owned.

TABLE I

Market category	Main products	Per cent of sales in 1978 by volume
Retail sector (service stations)	Motor gasoline Auto-diesel Lubricants	22
Industrial and commercial	Naphtha Aviation kerosine Auto-diesel Gas oil Fuel oils	65
Heating and agriculture (mainly by authorized distributors)	Motor products Regular kerosines Premium kerosine (paraffin) Gas oil (heating oil)	8
Special products/others	LPG Bulk lubricants Bitumen	5
Total		100

deliveries. Beyond these, the typical distribution network of a major oil marketing company will consist of its geographical chain of bulk product terminals, some wholly and some jointly owned and operated, some bigger and some smaller, and sited with regard to market density and accessibility to the optimized combination of transport modes to be selected (sea, inland water, rail, road, and pipeline).

THE MARKETING 'INSTALLATION' AND 'DEPOT'

Having outlined the nature of the typical distribution system as comprising a geographical network of both large and smaller bulk oil terminals, it must be noted that within the term 'petroleum installation' there is a further distinction between the 'marketing installation' and the 'depot'. In the IP Marketing Code these are defined as follows:

Marketing installation

Premises which normally receive their supplies direct from a refinery by ship, pipeline, or rail, and in addition to making deliveries direct into consumption in their immediate vicinity, may trans-ship both bulk and packed supplies by coastal ship, inland waterway barge, rail, or road to depots.

Depot

Premises which normally receive their supplies from a refinery or installation by road, rail, water, or pipeline, or by a combination of these methods, and deliver products directly into consumption in the area immediately surrounding the depot. (Transfer from a depot essentially will be by road.)

The facilities within an installation or a depot will themselves differ more by reason of scale, i.e. size and multiple number of tankage than by other factors, and the scale factor is reflected in the IP Marketing Code, separate requirements being set for safety distances, spacing of tankage, etc., depending upon which of the two categories is to be considered. For such a purpose there can be no hard and fast distinction, but by custom and usage it has generally been held

TABLE II
Movement of Components and Refined Products in 1978 by One Oil Major

Mode	Per cent of whole
General purpose tanker	14
Coaster	13
Barge	6
Rail	14
Pipeline	9
Road	44

that the upper limit of a marketing depot is one in which storage capacity for all classes of petroleum will not exceed 7000 m^3.

The physical facilities of an oil storage installation, whether an independent distribution terminal or depot, or a part of the storage and loading facilities of a refinery, comprise essentially means for bulk oil storage and blending; the receipt of vehicles and/or sea-going or inland vessels for conveyance; facilities for their effective loading and unloading and despatch, plus all the ancillaries and administrative services that allow these operations to proceed effectively.

The national distribution network of a major integrated oil company in the UK may well consist of some 40 or so installations, themselves also serving a secondary distribution chain as explained above. The various modes of transportation employed in the primary distribution step between the refinery petroleum storage installation and its marketing counterparts have been mentioned; transportation is the subject of other chapters. However, it may be of interest to note the breakdown reported by one major oil company in the UK given in Table II.

The percentage of the various transport modes utilized will vary with the particular network characteristics of the company, the product pattern marketed, and the economics involved in the different modes; one company modified its distribution operation between 1970 and 1978 by extending its trunk pipelines from 128 to 502 miles, with tonnage moving in this system doubling giving a corresponding reduction in road and rail movement.

INVENTORY MANAGEMENT

The determination of stock levels takes into account the minimum operating levels decided. These are based on the levels at which distribution diseconomies are identified, with minimum stock holdings set to allow for a very small probability of stock run out. The levels of each product take into account production lead time and its variability, distance of terminals from refineries, method of supply, alternative sources of supply, and required offtake levels. Stock holdings are integrated back into the forward production programme, and are controlled centrally as part of a complete supply system in which stock movements are reported back on a daily basis and projected stock levels monitored against actual turnovers. Within the overall supply pattern seasonal stockbuilding is also a planning factor to be taken into consideration.

Since maintenance of stock inventory level is a major cost which, it has been

stated, can account for over 50 per cent of downstream net operating capital at today's oil price levels, the provision of a national distribution network is aided economically by the use of shared as well as owned distribution terminals, and by exchange agreements under which pick-up rights at terminals owned by other companies are arranged, in return for corresponding pick-up rights.

The great increase in oil prices and the resulting lack of demand for some oil products that has caused a cutback in refining volume, and a rationalization both of capacity and pattern in the refining sector of the oil industry, with the closure of certain redundant refineries, has had its necessary counterpart in the examination of downstream oil distribution networks, with the closure of terminals and distribution depots, and more extensive use of exchange pick-up arrangements.

These activities emphasize the need for the petroleum installation and/or depot and its associated loading facilities to be built and operated to commonly accepted standards. The basic principles on which the design, layout, operation, and maintenance of such an installation are founded have been outlined in Chapter 32. The facilities required are determined by the classification of the petroleum stocks to be handled—Class I, Class II, Class III, or Unclassified.

TANKAGE FOR THE BULK STORAGE OF PETROLEUM

Above-ground Tanks

The majority of tanks in a modern installation are of the vertical cylinder type constructed of steel plates welded on site. Suitable codes for the design and construction of the tanks and their fittings are BS 2654 and API Standard 650. The plate material used on the smaller- to medium-sized tanks, say up to 80 ft or so in diameter, is normal mild steel. Above this size, the use of higher tensile carbon steels can show economies. In particularly large tanks, the use of low alloy steels on the lower two or three strakes may be justified on economic grounds.

Small horizontal cylindrical tanks may be employed for some purposes, but they are of a much higher capital cost per tonne. Their use is usually therefore limited to service tankage or small depots. They may be designed and fabricated in accordance with BS 2594 or similar codes. Where such tanks are elevated the fireproofing of their supports should be carried out, unless the risk of collapse from a fire is unlikely.

Tanks for operation at higher pressure than is covered by the above codes, or for low temperature service, e.g. liquefied gases, have their own special design standards.

Tank Foundations

The design standards BS 2654 and API 650 for vertical above-ground tanks give recommendations for appropriate foundations, which in general will depend on site conditions. The design chosen should provide drainage, avoid corrosion of the tank bottom, and give stability to the tank under all working and climatic conditions, including test loading. A knowledge of the ground

conditions should be obtained with respect to the allowable bearing pressure, which may set limits to height and also total and differential settlement. The latter is important in avoiding unacceptable stress in the tank shell and its connecting pipework (see below).

Foundations for above-ground vertical tanks may be of hardcore topped with sand and a 2-in thick bituminous macadam sealer. Successful use has also been made of the concrete raft pattern, and this is essential when piling is required. Various alternatives to these, embracing the use of a concrete peripheral ring and similar features have been used. As tanks increase in size the standard of the foundation tends to become more significant. The welded joint between base and shell is generally the most highly stressed part of a tank and any unevenness in support can become critical with the passage of time.

Controlled water loading of tanks during initial testing following construction is desirable to obtain regular tank settlement before tanks are placed in service (see IP Marketing Code, 1978: Section 3.3.1).

Buried and Mounded Tanks

Tanks meeting the foregoing standards for above-ground tanks may be buried or mounded, but are usually provided with an outer wall of concrete or similar construction for protection against earth or water pressure; and the design of the tank itself should be adequate for the superimposed loading.

Such tanks may also be constructed of concrete, usually with an inner steel lining. However, buried and mounded tankage can present problems in operation, inspection, and maintenance in regard to corrosion, access, and ventilation of galleries leading to tankside valves, gas-freeing, sludge removal and cleaning, and undetected leakage. All these combine to render them undesirable for petroleum storage.

Cavern Storage

Although not part of the conventional oil storage installation, the practice of storing petroleum and refined products in unlined underground caverns mined in appropriate rock formations, leached in salt beds or domes, or obtained by the conversion of disused mines, is carried out to a considerable extent, either for strategic stock-piling or for balancing peak demands, in countries such as USA, France, and Scandinavia. A section on this subject is included in the IP Refining Code, 1981.

Tankage Type versus Class of Product

Vertical above-ground oil storage tanks are of three main types:

(a) Fixed or cone roof tanks. These are usually fitted with pressure–vacuum vent valves when used for volatile, i.e. Class I products, but may be fitted with open vents for less volatile products.
(b) Floating roof tanks.
(c) Fixed roof tanks with an internal floating cover, or blanket (sometimes referred to as 'internal floating roof tanks').

The choice among these various types is dependent upon the volatility of the materials to be stored. As stated earlier, in Chapter 32, in the Institute of Petroleum Model Codes of Safe Practice, such a classification is made in terms of flashpoint into Class I, Class II, Class III, and Unclassified.

The type of tank roof to be selected is then a function of (1) safety, (2) size of tank, (3) economics of tankage evaporation loss and, possibly, environmental factors.

Fixed Roof Tankage (Fig. 1)

These tanks operate with a space containing air and vapour above the liquid. Thus in the case of a volatile class of petroleum (e.g. petroleum spirit, gasoline, etc.) some product loss will take place by the vapour expulsion which occurs at

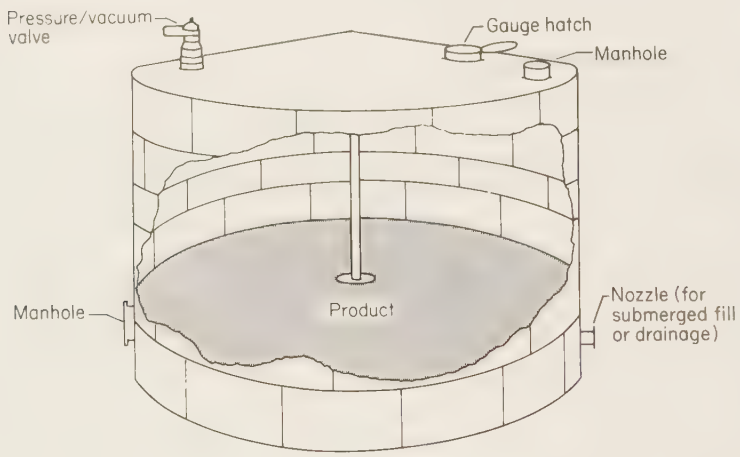

FIG. 1.

the time of tank filling, and in tank breathing during the standing storage period. To some extent this can be reduced with a fixed roof tank by fitting pressure and vacuum relieving valves. To this end in the UK fixed roof tanks can be designed for positive working pressures up to a maximum of about 50 mbar, and for slight vacuum not normally exceeding 6 mbar; such a design will permit the setting of a P/V relieving working range of up to 56 mbar, with the benefit as indicated in Chapter 35 of a reduction in breathing losses which is substantial compared to those of a tank open to the atmosphere. (Tanks for heavier products may be designed for atmospheric pressure only, in which case the are equipped with open vents.)

In addition to the use of P/V valves, since vaporization and emission are a function of temperature and variation of day and night temperature in cyclic breathing loss, reduced emission may be also gained by painting a tank and in particular its roof with a reflective (i.e. white or aluminium) as opposed to dark finish which absorbs solar heat more strongly.

Floating Roofs (Fig. 2)

Vapour losses of highly volatile products may be greatly reduced by the use of floating roof tanks. In these units the fixed cone or dome roof is replaced by one which floats on the surface of the product. Pontoons giving buoyancy are incorporated in the roof structure, and a vapour seal, of which a number of different types are marketed, is provided between the roof and the tank shell.

A further advantage of the floating roof tank is that in the rare event of a fire, it is generally confined to what is termed a 'rim-fire', i.e. involving the limited annular or seal area only, and this is fairly readily extinguishable by means of local foam application.

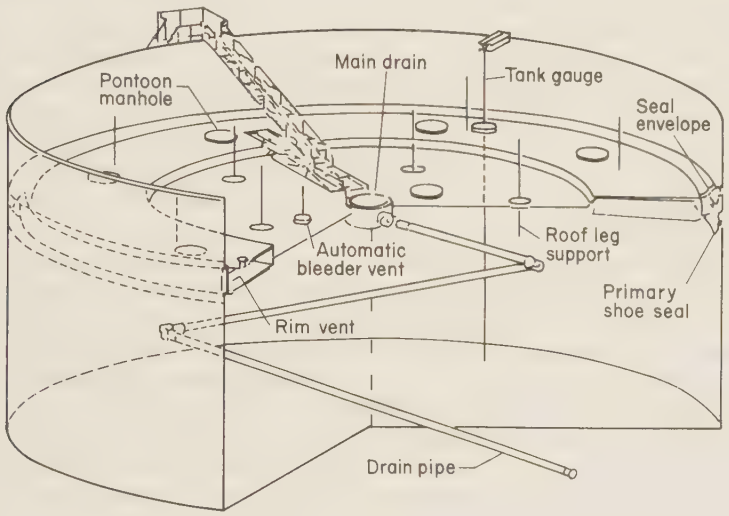

FIG. 2

In temperate climates Class I petroleum products, e.g. gasoline, may be stored in either fixed roof or floating roof tankage according to choice and availability, though with increased product value the latter is increasingly attractive and used. Class II petroleum products, e.g. kerosines, may be stored in either type of tank, although the vapour loss from both types is extremely low, and in the case of a fixed roof tank a simple (rainproof) open vent operating at atmospheric pressure rather than a pressure–vacuum valve is customary. For Class III or Unclassified products, e.g. gas oils or fuel, open-vent fixed roof tankage is customary.

Internal Floating Roofs, Blankets, or Covers

In cases where it is desired to convert a fixed roof tank, or where excessive snow loading or sensitivity of a product to contamination by the ingress of rain could preclude the choice of a floating roof, there are available a number of internal plastic or light metal 'blankets' or covers which have been used inside a

conventional fixed roof tank to float on top of the product, thereby reducing the product vapour content in the empty upper space of the tank, so that although breathing and filling displacement emissions still occur, they have a much lower hydrocarbon to air concentration than in an unblanketed tank. This raises the possibility of such air–hydrocarbon mixtures being within the flammable or explosive range; thus, while in some countries it is the practice to install P/V valves in tanks with internal floating covers, in the UK and USA it is more general that ventilating slits or vents are provided in the top of such a tank to assist in reducing the gas concentration in the space between the fixed roof and the internal floating cover to below the lower flammable limit.

In the selection of an internal cover, consideration should be given to both robustness of design and buoyancy, since there is a history of certain light-weight versions, e.g. often of the 'open pan type', sinking in service. The cover should be electrically bonded to the structure of the tank.

The whole field of tank vapour losses has in the past been poorly documented. Recently a number of tests have been undertaken in various parts of the world, from which far better understanding has become available (see section on evaporation loss in Chapter 35).

Tank Fittings

A stairway, either of external pattern or fixed spirally to the tank shell, must be provided to gain access to the top of any tank or group of tanks, together with roof-level footbridge walkways between tanks in the same group. Low-level shell manholes and roof manholes give access for cleaning and repair. Tank gauging or dipping is done through roof dip hatches in the case of fixed roof tanks, while floating roof tanks should be gauged and sampled from a gauging well, the hatch of which is at the top of the access stairway, thus avoiding the necessity for descent on to the roof. In addition to direct manual gauging, for all tank types and for ease of operation, a contents gauge which is readable from ground level may be provided and, as discussed in Chapter 35, in large installations a considerable economic advantage is gained by installing automatic tank gauge read-out to a central control point. This is increasingly attractive because it provides instantaneous stock positions and control where, for instance, tankage is fed by high flow rate pipelines or ship discharge. Such a system may operate on a radio link or by means of direct cable connection and give immediate tank depth readings, together with a temperature read-out where appropriate, e.g. for heated fuel oil grades. For details see Part 5 of the IP *Petroleum Measurement Manual* 'Automatic Tank Gauging'.

To permit water, sludge, and product to be drawn from a tank bottom below normal suction level a bottom sump and drain valve are advisable. The latter, in addition to any unused delivery and suction connections, should be fitted with blank flanges to avoid the possibility of leakage. All connections should be of the three-flange pattern or strengthened by compensating plates.

Tank Venting

Vents of the correct size (see API Standard 2000) should be fitted to fixed roof tanks. As stated previously for low volatility, Class II or III stocks, these

may be of the open vent pattern; for more volatile (Class I) stocks they should be of the pressure–vacuum type.

Emergency Venting for Tanks

Tanks should have some form of emergency venting to relieve excessive pressure in the event of exposure to fire. For floating roof tanks, the roof itself acts as the emergency vent. In a fixed roof tank emergency venting may be provided by a weak roof to shell seam; this will tend to fail preferentially to any other seam in the tank shell or bottom.

Tank Fire Protection

Because of meticulous safety measures tankage fires are very rare. Where there is deemed to be a particular risk of adverse consequences, it may be desirable to equip a fixed roof tank storing volatile material with a means of applying fire-fighting foam at either high or low level, and/or water sprinklers to provide cooling protection in the event of a fire on an adjacent tank. To achieve full effect from such sprinklers deflection plates are normally fitted to the tank roof periphery to deflect the flow of water uniformly over the tank shell. For many tanks such a fixed installation is unnecessary, since both flexibility and adequate prevention of escalation in the unlikely event of fire are achievable by bringing up mobile high-pressure fire monitors to direct foam or cooling water spray on to tanks as and where it is needed (see Chapter 32).

The simpler requirement for fighting a typical (i.e. rim) fire on a floating roof tank has already been mentioned.

Tank Heating

Heavy fuel oil and similar tanks which are to be heated are provided with external insulation cladding to conserve heat, and internal plain or finned tube heating coils with a thermostatic control to avoid overheating, and to shut off heat in the event that the liquid level falls below the heating coils.

Water Problems

Aviation products require a particular degree of quality control against water pick-up during transfer, this being achieved by means of floating suction assemblies inside the tank. Great care must be exercised to ensure that no water can be retained on the tank floor which may, for instance, be constructed so that there is a gradual fall to the centre which should be fitted with a small-bore water extraction pipe from the central sump.

Fuller details of tank fittings are given in the IP Marketing Code, Chapter 3 and in the Refining Code, Chapter 5.

Tank Compounds, or Bunds

Dependent on the product classification and site conditions each tank, or group of tanks, may require to be surrounded by a fire wall and adequately separated

from other facilities and the public boundary. The Institute of Petroleum Marketing and Refining Codes give full guidance on the extent to which this is required to be carried out for the different classes and their subdivision. Fire walls may be constructed in brick, concrete, or earth although brick is only economically suitable for small low structures.

Where the site conditions necessitate the provision of drains within the tank compound these should be controlled by a valve sited in a pit outside the compound wall. Under normal operating conditions this valve must always be kept closed to prevent the outflow of product which would occur in the event of a tank spill. Water and other liquids from the tank compound drain must be passed through the installation oil/water interceptor before discharge into either public sewers or water courses.

The Institute of Petroleum code 'Prevention of Water Pollution by Oil. A guide to preventing contamination of water discharged from oil users' terminals and other commercial premises', 1983, provides a guide to the operation and good maintenance of oil installation oil–water interceptors.

Corrosion Prevention

Corrosion prevention must be given serious consideration owing to the hazard, and the inconvenience and cost of repair work, necessitating the cleaning and gas-freeing of lines and equipment.

Corrosion prevention measures will include the following:

(*i*) *Storage tanks*

Following the shop preparation and the rolling of plates used in the construction of vertical storage tanks they may be primed to prevent corrosion taking place before the final coat of paint is applied. This priming may most effectively be carried out immediately following either shot blasting or pickling to remove mill scale and rust.

Prior to the laying of base plates on the foundation, protection to the underside can be achieved by the application of a bituminous material. Following erection the underside of the roof plates and support structure, which is particularly prone to condensation corrosion, should be treated.

(*ii*) *Pipelines*

Initial pre-erection corrosion of pipe can be prevented by the manufacturer's application of a bituminous paint. Internal protection of this type leads to a slight product discoloration in initial use and must never be used for aviation grade fuel pipework.

Following erection, above-ground pipework needs only normal external paint application. Extended paint life may be achieved by the use of micaceous oxide, zinc-rich, or other similar material.

Underground pipelines, where these are necessary, are normally protected by wrapping with asbestos felt or glass fibre, and the application of a bituminous compound. In poor ground conditions consideration should be given to the use additionally of cathodic protection by either the impressed or

the sacrificial anode system. Suitable insulating flanges above ground must be provided at points of emergence.

Loading Facilities

Loading of road and rail tankers at both distribution and refinery installations is a common operation.

The provision of roofed steel gantry structures giving easy access to the working platform where equipment is located is now considered standard practice. Access to the vehicle top is gained from the working platform by means of drop walkways, or latterly by self-levelling platforms which are considered to offer a greater degree of safety where vehicles of greatly differing heights are employed. The arrangement of these structures will be dependent on the limitations and layout of the general yard area.

Product may be transferred to the gantries by means of either overhead or underground piping, and where meter facilities are provided a filter unit must be installed to prevent damage by foreign matter. The great majority of terminals in the UK hold product under bond, and loading of petroleum products from a bonded warehouse is customarily by meter, the calibration of which is required to be checked at six-monthly intervals. For details see HM Customs and Excise Notice 179 M.

The product, when loading to road vehicles, may be dispensed through either a hose or a loading arm. Loading arms are either of the conventional or boom arm type. Arms are generally used for the higher loading rates. The conventional arm is such as will allow for use at either side of a gantry, whereas the boom arm is often restricted to a single side. Avoidance of splash loading (see Chapter 32) is ensured by extending the drop pipe to the bottom of the vehicle tank or compartment to be loaded.

Loading Rates and Pump Capacities

The economics of rail feeding are, to a point, dependent on the quick turn-round of the train. To this end pumps of a size suitable for obtaining an appropriate turn-round time are provided. Good turn round is also required in road tanker loading, and in recent years loading rates have been progressively increased by the use of larger diameter loading arms such as will keep flow velocities still within acceptable levels for the avoidance of risk from the generation of static charge. A common provision at the modern road tanker filling gantry is the 4-in diameter loading arm, capable of a rate of filling of about 2500 litres (500 UK gals) per minute, and a loading period of approximately 20 minutes. In some cases loading arms of 6-in diameter, with a rate of 4000 litres per minute, are being installed.

For rail loading, where rail cars of 100-tonne gross laden capacity are common, loading arms of up to 8-in have been installed for handling white oil products; loading rates with such equipment may range from 4500 to 6000 litres/minute (say 210 to 300 tonnes/hour). For fuel oil, arms up to 10-in dia are being utilized, with loading rates of 11 000 litres/minute (550 tonnes/h). Where a loading pump is designed to serve more than one loading arm it is essential that some form of maximum flow rate control device is fitted in order that the

prescribed flow rates are not exceeded. A preset device which ensures that overfilling does not take place, may be coupled to the loading meter, particularly where high flow rates are employed. In addition, ticket printer mechanisms to facilitate accounting procedures are usual.

In recent times pump/loading facilities have been installed on the 'cascade' system. By this means a number of pumps and loading arms serving a single grade are interconnected incorporating 'logic' control. This allows pumps to be brought into operation as required on the basis of the number of arms in use at any one time. The control ensures that pump operation is set on a strictly rotational basis, thereby achieving equal utilization of all units.

Trends are for the greater use of computers for all but the smallest installations. By these means customer information, site limitations, hours of delivery, etc. can be tabulated, and full and efficient vehicle utilization achieved in the routing of loads to different customers. The system may at the one end be coupled to loading instructions transmitted to gantries and at the other by data link transmissions to a central account preparation computer. Such systems may also be linked to a refinery and product requirement computer, whereby actual offtake of product may be instantaneously reported to a central control point and the production/distribution programme be correspondingly adjusted.

CONTAINERS

While the modern trend in the oil industry is to make deliveries, wherever possible in bulk in order to obtain the utmost economies in distribution costs, packages are still extensively used for lubricating oils and greases, which must be available to the ultimate consumer in a great number of different grades, and for various special products, such as anti-freeze solutions, etc.

In most countries the usual practice is to concentrate lubricating oil and grease blending and packing at separate plants designed for the purpose. But in some cases the filling of packages of motor spirit, kerosine, gas oil, etc., may form a part of the installation's operations.

The various types of packages are generally divided into two groups, returnable and non-returnable. Returnable packages would normally include heavy and light steel barrels and all-welded drums of varying capacities, and the non-returnable type would include a variety of different containers ranging from lightweight barrels, silicone-lined paper sacks for bitumen, and pails and buckets for grease, to sealed tins, plastic bottles, cartons, or sachets for automotive oils.

Returnable packages are cleaned and reconditioned on their return from customers and, depending on their condition, may be down-graded to hold some other product, e.g. lubricating oil packages may subsequently be used for gas oil, fuel oil, or bitumen. The use of a lacquer lining helps to prevent internal corrosion.

In non-returnable containers the last few years have seen the introduction and use of a lightweight non-returnable steel barrel. In the range of smaller sizes plastics are being increasingly used as an alternative to the tinplate container which, however, still remains popular in some countries. Small

plastic containers for motor oils take the form of blow-moulded bottles or cylindrical cans with a metal top.

Overpacking is generally required for containers of 5 l or smaller. Traditionally this takes the form of a cardboard carton, but two recent developments in this field include shrinkwrap and the wrap-round carton. With shrinkwrap the containers are assembled in cardboard trays, wrapped in a polyethylene non-slip film then pressed through a heat tunnel to form an attractive tightly knit pack. The wrap-round carton is made up from a flat cardboard blank; the wrap-round machine is automatic and can operate at high filling speeds.

Packages may be filled in a variety of ways, the actual method employed being dependent on local conditions and government regulations. They may be filled by weight or by volume.

Volumetric fillers vary considerably in type. They range from the semi-automatic temperature-compensated unit, complete with its own air eliminator, strainer, motor, and pump, to a simple measuring device which, on one stroke, draws in an exact quantity of liquid and, on the reverse stroke, discharges the measured quantity into the waiting container.

Another well-known method of filling involves the use of multi-head fully automatic machines. In this type, the relative positions of a series of moving nozzles to a fixed cam make it possible to fill a variety of small packages to a given height.

In some areas considerable advances have been made towards full automation, particularly in regard to the filling of small packages, i.e. cans and tins, and machinery is now available which permits the various operations of decorating, filling, capping and sealing, and packing to be carried out automatically once the empty packages have been fed into the filling line.

Apart from automatic filling lines, various other types of mechanical devices are being increasingly employed for the handling of packed products. Handling accounts for a high proportion of the cost of finished products in this field, and the use of mechanical aids can effect considerable economies in labour, time, and storage space.

The pallet or stillage and the fork lift truck are the most widely used pieces of mechanical handling equipment. These, together with suitable racking, permit optimum use to be made of available storage space. Pallets are produced in a variety of shapes and materials in order to suit the different types of package or container which may be handled in the installation.

Guidance as to the layout required for the storage and handling of packaged petroleum products is given in Chapter 3 of the IP Marketing Code, and in the European Model Code, Part 2.

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Automatic Control and Instrumentation

By J. E. MILLER, B. REYNOLDS and S. W. BARBER

INTRODUCTION

Automatic controls have been used in refineries for decades and continue to increase in importance and complexity. The drive towards more efficient, flexible, and safe production is bringing with it more and more sophisticated measurement and control systems, which are at the heart of the refiner's operating strategy. The installed cost of instrumentation on a refinery continues to rise, and is now around 11 per cent of the total cost of process equipment. Its benefits include increased plant efficiency and profitability, with sufficient safeguards to allow a reduction in operations manpower. The input to the control systems may be considered to be monthly or quarterly production targets and programmes, together with product quality specifications. The output is a series of interrelated signals which steer the plant towards its optimum state, and at the same time assure its condition, while that of associated equipment is kept within safe mechanical limits.

Several phases in the development of measurement and control are discernible and these are:

(i) Achievement of dynamic stability in a continuous process.
(ii) Achievement of output continuously controlled to within required limits of product specification.
(iii) Integration of several interconnected plants, and maintaining control so that the consequential effects of an upset in one of the plants are minimized in others forming part of the chain.
(iv) Improvements in the operability of plants which may include multivariable control, constraint control, and analytical control.
(v) Protection against equipment malfunctions, internal plant failures, upsets in utilities supplies, and abnormalities in the feedstock.
(vi) Optimization of the process conditions so that the profitability is at a maximum.
(vii) Developments in visual display units which provide the operator with a concentrated over-view of the status of the plant variables.
(viii) Provision of reserve instrumentation to act as a fall-back if there is a short-term failure in the main-line equipment, so that the plant can continue in operation, although less effectively.

The growth areas are likely to be the even more extensive use of field mounted analysers; on-line digital computers wholly engaged in direct digital control of a plant or in supervisory control of a complex; and more emphasis on the interrelationship between the plant computer and the higher level computers responsible for the refinery and the overall operation of the company manufacturing facility. Moreover, whilst the principal impact of measurement

and control was originally in the process, it is now extensively used in off-site operations, transportation, cross-country pipelines, and production platforms.

Sometimes precision of measurement may be of less significance for plant control than repeatability, but is very important in the reduction of refinery losses, which can be more readily tracked down to their source, in the assesment of plant yields and in providing a firm basis for fiscalization. Great efforts have therefore been made in recent years to develop equipment and standards for both accurate static and dynamic petroleum measurement. (See *Petroleum Measurement Manual.*)

Control Rooms

At one time each plant had its own dedicated control room, but in modern installations these are usually combined. A central control room will be provided for all the process facilities in the smaller refineries and chemical plants, or for major sections or areas in larger sites. These buildings are located in a non-hazardous area on the periphery of the plants, and house more than just the control panels and operators' consoles. They also comprise the plant computer room, together with associated facilities for air conditioning; an auxiliary room for cable terminations, transducers, alarm units, and power supplies; the operators' changing room and showers; and possibly a suite of offices and a training lecture room. In some circumstances it may be deemed necessary to have a reinforced control building. This is with the intention of providing sufficient protection for operating personnel and instrumentation, so that they remain able to function and take emergency action in the remote event of a plant explosion.

Manpower

Increased use of automation has brought about significant changes in the manpower pattern within the petroleum industry. Unquestionably with a greater degree of instrumentation operating crews have been gradually reduced, although there is always a lower limit of manning for general plant safety and to deal with emergencies. There has also been a decline in the number of laboratory staff due to the increased effectiveness of quality analysers.

These reductions in operating and laboratory staff have been offset by the greater number of instrument technicians and specialists in analysers, microelectronics, and computers that are required to deal with the latest advanced equipment. Here technical knowledge, experience, and training are more important considerations than numbers. There is a potential shortage of people with the right skills, and this may become even more apparent in times of a buoyant economy. Increasing efforts are therefore being made to interest the younger generation in the possibilities of employment in the instrumentation field.

Plant

Automatic control of a process plant aims at achieving: dynamic stability of a plant, steady operation at what are regarded as the most efficient operating

conditions, under the prevailing circumstances, and avoidance of waste by keeping product quality within specified limits.

Continuous process plants have evolved since the early 1930s by using pneumatic controllers, electronic controllers, and more recently digital computers and distributed microprocessor based control instrumentation systems. The improvements made possible by the real-time use of distributed digital systems for the direct control of plants or complexes have been justified by the ensuing profitability, and operational reliability (see Thurston, 1979). Such systems are capable of more than conventional control to achieve dynamic stability, and are increasingly involved in the role of automatic plant management. Real-time networks incorporating production quality control, optimization strategies, and linear programming are able to influence operational decisions, and indeed to influence directly the digital controller modules, causing actual changes to be made to the control valves on the plant.

Safety

The ability of a computer to scan large amounts of information, and make virtually instantaneous logical decisions based on previously contrived programs is of great benefit to plant safety. An operator could not hope to compete on equal terms, although there will be many situations where he will have the advantage because the circumstances will not be those for which the system has been designed and has some prior knowledge. However, computers are not infallible, and what is important is to guard against a fault in the equipment which could have devastating effects without a safety protection system. This should be completely independent if it is to be an effective watch-dog. Furthermore, to design and install such a system is not sufficient; a planned routine of frequent checking by competent personnel to make sure it is fully alert and operative is vital.

Advantages of Digital Systems

Digital Systems cover the range of functions from single-loop controllers, multi-loop controllers, and operator VDU-based work-stations, up to central supervisory or direct control digital computers.

The digital loop controllers are generally dedicated task microprocessor devices performing a range of closed-loop control and computational functions. Several such controllers may be applied in a modular fashion, and interconnected via serial or, in some cases, parallel, communication links for operator work-stations and computer system access. The loop controllers normally perform alarm monitoring on in-coming and calculated signals, and hold all information related to the process signals, signal conversion, and control factors in their own local memories for access over the communication links.

Digital control permits drift-free control action to a consistently high level of computational accuracy, and offers the additional benefits of simple restructuring of the control strategy and modification of the control equation parameters. When implemented in several single-loop or multi-functional process-unit controllers, the risk of total failure of the control function is

significantly reduced when compared to the use of a single process control computer.

Storage of process parameter history in the system memory permits the recall and display of process trends in graphical or tabular format on VDU-based operator work-stations for periods varying from a few minutes to several days, or even longer in systems with bulk storage devices.

The control equations used are generally wider in scope than conventional three-term algorithms, and accommodate non-linear relationships, dead-time compensation, and may also provide time-related and logical sequential operations.

Digital computers within a Distributed Digital System are primarily employed to take advantage of their bulk memory, communications facilities, and the additional processing power for complex and plant-wide control strategies combined with data analysis, and reporting. Many also support the use of high-level languages for more flexible implementation of control and specialized tasks. The increasing use of report-by-exception techniques in the distributed instrument systems, plus alarm reporting at the operator work-stations, frees the computer from its previous burden of scanning for all alarm conditions on all process parameters.

ON-LINE QUALITY ANALYSERS

The rapid expansion in the use of on-line quality analysers has been brought about by several factors. Probably the most significant of these is the advantage of being able to operate the plant so that the product is closer to the quality specification than with intermittent manual samples taken to the laboratory for analysis. This is only part of the justification for installing analysers, and there are several other reasons. It is now accepted practice to have integrated process units, less intermediate storage capacity and more in-line blending, sometimes delivering direct to product carriers or pipelines. All of these provide less opportunity and time for corrections to be made to the quality of the run-down stream, and hence a constant supply of information from the on-line analyser is extremely useful and valuable. The necessity for reprocessing may be minimized, and more frequent adjustments can be made to the plant conditions, which may be necessary arising from variations in the feedstock, or because there may be a requirement to make different product grades.

Improved Quality Control

The inherent limitations in laboratory quality control are now fully recognized. Not only is there a significant time lag between drawing a sample and having the analysis results available, there is also a considerable risk that the composition of the sample may change after it has been taken and before it is analysed. Preference is therefore for an on-line quality analyser where it is essential for the operator to be kept continuously informed of any deviations from specification. Moreover, it is now sometimes possible to include the signal output from the analyser in a closed-loop control system to reset a plant parameter automatically to control the product quality.

Thus production losses, caused by over-refining or over-blending to ensure

meeting critical specifications, can be minimized, and often substantial economies will accrue from less severe processing conditions or from reducing the usage of an expensive blending component. Manufacturing limits can in many cases be more closely controlled as a result of using on-line analysers, but it is a prerequisite that there must be the same confidence in the analyser result as there is in the corresponding test result. (See Code of Practice for Calibrating Process Analysers.)

Of course it is also important that failures of the analyser are rare, and if they occur are only of short duration. The full benefits of having an expensive item of equipment will not be realized if there is frequent recourse to manual sampling and laboratory analysis.

Whilst the digital computers referred to earlier in this chapter have in themselves great advantages the ultimate test of whether the plant is on-grade is often the result from the on-line quality analyser. Hence the cost-benefit of advanced control systems may be very much dependent on the effectiveness of the analysers.

Reduced Operating Costs

Fuel costs for process heaters and boiler plant can be minimised by running to optimum excess air conditions using oxygen analysers. Types which offer a probe into the stack, rather than having an external sampling system, are now available from several manufacturers. Although they can present problems due to the arduous service conditions the oxygen content is available more quickly and hence immediate adjustments to firing conditions can be made either manually or automatically.

Reductions in chemical and catalyst consumption, and in corrosion, may also be achieved through the use of analysers. A typical example is the use of pH meters to control ammonia injection into the overhead systems of crude oil distillation units.

Pollution and Safety Requirements

In these days of increasingly stringent environmental and safety requirements, analysers are available to detect operational upsets which could lead to pollution and toxicity hazards. Typical examples are the use of sulphur dioxide analysers for monitoring atmospheric conditions, oil-in-water analysers for monitoring the oil content of water effluent streams, and hydrogen sulphide alarms for personnel protection. This gas is especially dangerous due to the loss of olfactory perception of its presence at lethal concentrations.

Requirements for Analyser Installations

An effective analyser must be robust, give readings which correlate with standard test methods, be capable of operating for long periods without maintenance and meet the safety requirements for the area in which it is installed. The performance of commercially available equipment has improved considerably over the past few years.

During the early years of installing analysers there were many difficulties,

and the on-stream time, reliability, and accuracy were not sufficient to gain the operator's confidence in the readings. Hard lessons were learnt, especially in the field, as often the analysers would work satisfactorily at the manufacturers, and soon failed to function or give reliable results when connected to plant streams.

The analyser itself has to be very carefully designed and engineered, based on a sound and unequivocal physical or chemical principle of measurement, and using only proven mechanical and electronic components in its construction. It is then essential to provide it with a sample which is clean, non-corrosive, and free from any undesirable contaminants which can either interfere with the internal sensing devices, or produce incorrect readings. Consideration must also be given to the pressure, temperature, and flow rate in the sampling line, and if necessary to adjust these to acceptable values for the analyser. The sampling point must be selected to provide a satisfactory and representative sample, and this must be piped to the analyser with the minimum of delay. Sometimes only a single sample line may be all that is required, but often a fast circulating line, together with a sample pump, will be necessary. A sampling conditioning system must then be installed between the sample line and the analyser.

It has now become the practice to install groups of analysers in small buildings in the plant area, which are generally known as analyser houses. This concentrates the instruments in one place where they are fully protected from the environment, i.e. sun, rain, wind, frost, etc. and where they can be maintained *in situ*. The usual practice is to purge the analyser house continuously with air from a safe area so that the atmosphere is safe under normal circumstances, and technicians can work on the analysers without removing them to a workshop. Sometimes analysers are packaged in a completely self-contained product quality monitoring unit, which includes sampling systems, heating, lighting, ventilation, and safety devices, all built into a transportable walk-in housing on a steel skid base. With this approach functional tests on the analyser systems may be made at the factory before delivering to site, thus reducing the commissioning and start-up time.

An important consideration is the response time of the analyser system. First, the analyser test frequency must be sufficiently high compared with the plant characteristics so that the quality trends will be followed. Secondly, the overall time constant for the system, including the sample distance/velocity, analyser testing time, and the response of the control system, must be short compared with the plant response time, particularly if it is intended to use the analyser signal in a closed-loop control system. For these circumstances sensing devices which can be directly installed in the line have an advantage, and there may be control problems where the analyser is installed in an analyser house and the sample lines are rather long.

Application of Analysers

Gas chromatographs are widely used, especially in chemical plants for making analyses of selected components in a hydrocarbon gas or liquid stream. They may measure either one component or several components in a single stream, or be multi-component and multi-stream. The detector signals are in the form of

component peak heights, and it may sometimes be useful to provide a peak-picker to convert these into a continuous reading. Several types of detectors are available depending on the components and their concentrations. A reliable source of carrier gas is essential, and the supply bottles will usually be installed on the outside wall of the analyser house. The programmer may either be installed in the analyser house or the control room, depending on safety and maintenance considerations, and in more sophisticated systems its function may be taken over by the plant digital computer.

Viscometers are widely used on lubricating oils and fuel oils, especially on in-line blending, although they are also very useful on residue streams to indicate loss of middle distillates. All continuous viscometers measure viscosity in absolute units which can cause problems when correlating with laboratory instruments which measure in kinematic units. If large variations in density are expected, either several calibration curves should be provided or a continuous densitometer should be installed to provide automatic compensation.

Several different types of analysers are available to measure the physical properties normally used for product specifications. These include boiling points (including initial and end points), cloud point, flash point, pour point, and vapour pressure. Applications are usually to gasolines and middle distillates, and much ingenuity has gone into designing instruments which can operate continuously and give good correlation with the laboratory standard test methods. In most cases good results are obtained, but problems can sometimes arise where efforts are made to extend the use of analysers to outside their normal working conditions, e.g. flash points of fuel oils.

Moisture analysers for the water content of platformer recycle gas have proved extremely useful in prolonging the effective life of the catalyst. They are required to measure down to very low levels of moisture, e.g. 15 parts per million, and a considerable amount of effort has gone into devising an accurate calibration standard.

An interesting application is the on-line measurement of octane rating for gasoline from in-line blending systems. The product gasoline originating from the blender header, and the target gasoline from a storage tank are continually compared in a CFR engine installed either in the laboratory or in an analyser house. It is then possible to adjust blend recipes, if the need arises, during the in-line blending operation. For measurement of the octane number of run-down streams from reforming plants use is also being made of analysers employing inferential techniques.

In addition to the above examples analysers are used on many other processes, including those for lubricating oil production, alkylation, isomerization, catalytic cracking, hydrocracking, boiler feed water, and furnaces.

DISTRIBUTED DIGITAL CONTROL SYSTEMS IN RELATION TO PLANT CONTROL AND MANAGEMENT

Analogue control computing has been used in pneumatic form from the early 1930s, and in centralized miniature analogue electronic controllers using transmitters from the mid-1960s. Digital control computing was introduced in 1959, using centralized computers interfaced via analogue/digital signal conversion modules in both Supervisory Setpoint format and Direct Digital

Control (DDC) format, which by-passed the analogue control element and influenced the control valve position directly. In 1975 Distributed DDC was introduced using microprocessor-based control computing modules performing DDC on small numbers of control loops interfacing directly to the plant signals without intermediate analogue controllers. Distributed DDC systems comprised several such controller modules connected via communication links to operator work-stations consisting of a CRT display, keyboard, and digital processor, and frequently also to higher level digital computer systems. The current generation of distributed controllers are now providing a range of logical and sequential capabilities, in addition to linear and non-linear closed-loop control and mathematical computation. The tasks of handling interlocks, automatic strategy switching, automated start-up and shut-down, and batch control are executed at a level of complexity which previously required a process control computer.

The advantages of distributed digital control result from the distribution of functions and devices, and of the digital aspects of control and communications. Separation of functions into data acquisition, control modules, and display stations minimizes the risk of total system failure, and eliminates dependence on a single digital computer for essential plant control and operator display requirements. The communication links inherent in such systems permit the operator display stations to be several kilometres distant from the controller module when required.

The detail of the functions to be performed, and the interactions between the functions of a distributed digital controller module need not be fully defined until the final stages of the instrument system procurement cycle, giving a great deal of flexibility in the project engineering, and minimizing the number of different types of controller hardware modules to be held as spares. The electronics performing the interface between plant signals and the controller functions are either standardized to a fixed set per controller module or are chosen for the specific application and assembled into the controller module cabinet.

Digital control offers consistent drift-free computation, supported by alarm monitoring, signal linearization, mathematical routines, and accurate time-dependent control compensation. Multi-loop strategies can be transferred smoothly from manual intervention to fully interactive cascade control. The implementation of digital control in distributed systems provides these benefits at the instrument and operator work-station level, reducing the task of process monitoring and complex control in the process control computers which are steadily assuming more of the role of real-time plant optimization and management information reporting.

The operator interface CRT display techniques allow a single loop or the status of up to several hundred process variables to be presented on the one screen, and consoles comprising several such screens have essentially replaced the rows of panel-mounted instruments in the control rooms for distributed systems.

Distributed DDC Systems have utilized the technology of the microprocessor to ensure high standards of data communication integrity, and to advance significantly the level of self-testing and diagnostics at both the instrument and operator interface. The diagnostic routines extend beyond the instrument to

validity-testing of the incoming process measurements. Very high levels of reliability are achievable using simple redundancy at the operator interface and communication links. Automatic change-over redundancy is generally applied for the distributed DDC controllers when the reliability required for critical situations is not met by the distribution of the risk of system failure through using several controller modules.

The distributed systems inherently provide the basis for more reliable, consistent, and accurate reporting of useful data from the processing complex, and go some considerable way towards meeting the system documentation requirements of management by self-documentation print-out routines. As the distributed systems continue to evolve with more processing power at the instrument and operator interface level, the quality of the data for the operator and manager at the higher levels within the systems is expected to improve even more significantly.

OFF-SITE OPERATIONS AND HANDLING

Whilst perhaps in the past the application of advanced instrument and control systems in off-site operations has lagged behind the process plants it is fast catching up. On the upstream side of the processing plant off-sites comprise the facilities for importing the crude oil feedstocks, either from jetties or pipelines. On the downstream side they comprise product tanks, in-line blending either on the run-down streams or from the component tanks, and delivery systems for the various exporting routes, i.e. road, rail, barge, ship, or pipeline. The entire complex of jetties, pump houses, blending systems, and storage tanks may be the responsibility of one central control room.

In-line blending is now well established in modern refineries. Accurate blending of finished gasolines, gas oils, and fuel oils has proved to be profitable by reducing product 'give away', and at the same time effecting savings in capital investment on tankage and piping. Less intermediate product storage is required when direct blending into plant run-downs is possible, and it is becoming increasingly acceptable to blend direct to ships and pipelines, again saving tankage. There may be up to eight or more component and additive lines connected to the blender header, with the flow rate either governed by the major component stream or by a master signal. The key to successful in-line blenders is the choice of the meters, which are usually turbine meters for white oils, and positive displacement meters for black oils. It should be mentioned that experience has shown that these meters should only be used for blending, and not for fiscalization where another set of meters with proving facilities should be provided. The early systems had an electronic digital controller for each component meter and control valve, but these have now been replaced by a microprocessor or mini-computer, with better control and display facilities. Of course the operational success of an in-line blender does not rest exclusively with the instrumentation; component tanks must be homogeneous and careful attention must be given to the formulation of the blend recipe. As a final check each blender header will usually have a full complement of appropriate on-line quality analysers, i.e. octane rating, distillation, cloud point, viscosity, and density, to check that the quality of the product is to the market specification.

Occasionally these may be used to adjust the proportions of the components and additives during the blending.

The fiscal obligations in the bulk handling of dutiable products provide scope for an essential contribution by instrumentation in the petroleum measurement field. Both static and dynamic techniques are used in such a way as to provide accurate quantity data without constraining operations. For crude oil measurement the flow rates from jetties are usually high so as to reduce demurrage charges, and hence it is more practicable to measure receipts in the storage tanks by automatic level and temperature gauges. These are now available giving digital readings to within a few millimetres for level and fractions of a degree for temperature. Signals from them can be fed into a mini-computer together with the tank calibrations to provide conversions into standardized volumes for accounting purposes. The presence of water in the crude oil can present problems in measurement, of which more later in this chapter. For the measurement of products metering systems are usually preferred, especially as they can make it unnecessary to dedicate tankage to a single means of exporting products. Again, either turbine meters or positive displacement meters are used depending on the viscosity of the product, and nowadays both are fitted with pulse transmitters rather then mechanical counters to reduce meter slip. Automatic temperature compensation using a resistance thermometer and a microprocessor is provided for heated oils, and special care has to be given to the security and fidelity of the electronic system.

Meters have to be proved to the satisfaction of the authority levying or making other fiscal charges, before they are accepted as the basis for this purpose and at frequent intervals thereafter. Depending on the size of the metering installation the prover may either be a proving tank or a proving loop, on which more information is given later in this chapter. The proving loop may either be a permanent feature of the system or be of the mobile type transported to the site when required. Irrespective of the type of prover its calibration must be traceable to national standards, and be verified from time to time. For solid or semi-solid products such as sulphur and bitumen, and for LPG transfers to road and rail, weighbridges with load cells and electronic displays are generally used.

Remote operation of off-site facilities from the central control room is carried out by electrically operated valves, mixer, and pump controls, etc. To provide the operator with information on the status of these controls, and the line-up of the system, large mosaic panels came into use and served the purpose well for several years. With modern developments it is now possible to replace these by visual display units with keyboards for the operation of the pumps and valves. These visual display units can provide a series of coloured graphic diagrams which can be selected by the operator for each section of the oil movements area. They take the place of the mosaic panel but occupy far less space, and are easier to modify when changes are made to the piping system.

More and more use is being made of mini-computers for such functions as control of in-line blending, monitoring tank levels and movements of oil, status alarms, control of remote facilities, logging, and reporting, and linking with other refinery computer systems for information transfer to scheduling and accounting systems. One example of the extent to which such systems can assist operations is where a tank movement is monitored to check that any change in

level during a transfer corresponds to what is expected from other data, and where by assessing the change in a given time in relation to tank capacity an early warning can be given of possible over-filling.

Automation is extending into the loading facilities for road and rail vehicles, and this has been encouraged on the one side by the increasing intensity of operations and higher flow rates, and on the other side by developments in microprocessors and mini-computers for data capture systems. In the newer designs of loading racks even more attention is being paid to such matters as metering accuracy, automatic temperature compensation, and less possibility of loading errors. Rail loading gantries have been built with the capability of loading rail cars much faster than before, and these depend to a very great extent on instrumentation.

One aspect of the engineering of automatic control and instrumentation for off-sites is the need to provide continuous monitoring of vibration and bearing temperature of running equipment to give early warning of any incipient malfunctioning, together with heat or smoke alarms. Another is the electrical cabling for all the signals that are transmitted to the control room. Direct wiring of each signal via individual cores of a multicore cable is one approach. Another more recent development is to have a series of remote units into which each measurement sensor or control device is wired. These units have a microprocessor that communicates with a master station at the control room via a twisted pair highway.

The cost of installing all these new automatic control and instrumentation systems is high, but can be justified by considerable manpower savings, product quality improvements, reduction in refinery losses, conservation of energy, reduced capital expenditure on tankage, better utilization of equipment, more operational flexibility, and improved information for management.

MARINE AUTOMATION

The last decade has seen a continuing expansion in the use of instrumentation and control equipment in commercial shipping, particularly within the machinery spaces where the principle of unmanned operation for extensive periods is now well established. The major impetus for this development has been the rapidly increasing running costs experienced by the shipowner, of which the two principal items have been the cost of fuel and the cost of manpower. Improving the standard and level of instrumentation fitted can help to reduce costs substantially in both these areas.

Enhanced instrumentation to permit a reduction in manning levels is seen principally in the wide application of electronic equipment for supervisory and monitoring services. The equipment provides effective control of the engine-room machinery, together with comprehensive detection of faults and consequent alarms. The use of such equipment, which may have limits on its operational environment, together with the need for centralized control facilities for unmanned operation, has led to the general adoption of insulated and air-conditioned control rooms in a parallel philosophy to that employed for onshore process plant.

It is the control room that is at the heart of the unmanned machinery space or

UMS notation as provided by Lloyd's Register of Shipping and other classification societies. Essentially, it is the automation that acts as engine-room watchkeeper, freeing the engineering staff to carry out the required maintenance, and permitting the shipowner to reduce the number of engineers carried. Should an alarm be generated within the machinery spaces a duty engineer will be summoned to the control room where the fault or failure is displayed and whence the engineer can initiate manual or automatic corrective action.

The centralized control room provides the environment necessary for the successful operation of the equipment, together with a clean and comparatively quiet working area for the engineering staff from which the operation of the machinery may be controlled. The adoption of the centralized control station has also produced a change in the use of transmitted measurement systems to replace the previous arrangement of local gauge boards containing direct-reading instruments with live services, steam, oil, water, etc. piped to them. The increased costs associated with transmission are more than compensated by the reduced safety hazard.

Both pneumatic and electronic transmission systems are in general use for the measurement of process variables, with a clear trend to the increasing adoption in the marine field of the 4–20 mA standard. However, the final control element is still usually pneumatic with diaphragm valve actuators in general use for modulating duty.

Thermocouple and resistance thermometers are both widely used for temperature measurement, often connected to multi-point indication, with a preference given to thermocouples wherever vibration is encountered.

Hydraulic transmission is also widely used, particularly on tankers, where on grounds of safety as well as convenience, hydraulic actuation for valves in cargo tanks, pump rooms, and deck areas is commonplace, usually operated remotely from a centralized cargo control room where a mimic display of pipelines, tanks, and pumps is provided on the operators' console.

The use of electro-hydraulic deck machinery, such as winches, is also becoming more widespread.

Alarm systems have been used at sea since the first days of steam, and their development has generally followed in parallel with land applications. Today the trend is towards more comprehensive alarm coverage, but continuing to use equipment and technology first proven in land applications, 200 to 300 alarm points now being usual on an oil tanker.

Alarm systems using annunciators of both the individual window and VDU display types are commonly used. However, with the increasing numbers of alarm channels in modern applications VDU displays are often used to provide economy of panel space.

Most alarm systems incorporate an event recorder, and in the more sophisticated systems this can take the form of an automatic typewriter providing data logging and system information as well as a full record of alarm events.

Unmanned operation has led to the introduction of levels of alarms, a first-stage alarm of an off-normal state is followed by the automatic start up of standby machinery before a final plant trip alarm level is reached. Alarms are additionally grouped into categories and displayed on the Bridge, such that the

Bridge Watchkeeper is informed if the engine-room event will lead to a loss or reduction of propulsive power or manoeuvrability.

This grouped alarm information is often displayed in public rooms, as well as in engineers' cabins where an engineer call-out alarm panel is provided to inform a designated engineer of the engine-room alarm condition.

Alarm coverage and condition monitoring of plant items in hazardous areas, such as the pump room on an oil tanker, is also increasing. Marine practice is following industrial precedents for electrical transmission. However, the process plant zonal concept for electrically-safe systems has not yet won universal acceptance. The relevant national and international regulations have defined marine practice for oil tankers, but these are not necessarily applicable to other ships which may have hazardous areas. The regulations for tankers define specific hazardous areas and the equipment allowed, together with the categories of explosion protection permitted in those areas. Pump rooms, for instance, may contain only IS equipment apart from flameproof luminaires and deck areas, although not classified as zone 1 are only permitted to have zone 1 equipment fitted (see Bailey).

Ship-owners are increasingly aware of the steady escalation in fuel costs and a more variable fuel quality, and the serious impact these factors have on the running costs of their vessels. The high fuel costs are immediately apparent, but no less important are the hidden extra costs imposed by lower fuel quality in terms of wear on plant and machinery breakdown. The rising costs incurred have established a modern trend to the fitting of more analysis instrumentation and plant performance and condition monitoring equipment than was historically the case.

Salinity sensors have long been fitted to domestic freshwater and feedwater systems. More recently both alkalinity and dissolved-oxygen monitors have been fitted to boiler-feed systems but without consistent success; vibration continues to be a problem on some types. Oxygen analysers, however, for the monitoring of boiler flue gas for good combustion and for the monitoring of the inert gas blanket in the ship's cargo tanks are now well established. Both sampling types and the zirconium direct-reading oxygen analysers are in common use. Portable sampling oxygen analysers and explosimeters are also widely used to monitor atmosphere in cargo tanks and enclosed spaces before entry by personnel. Dew-point measuring instruments are sometimes fitted to boiler exhausts, and humidity sensors are often fitted to the instrument air system.

Additionally international regulations now coming into force, govern the fitting of oil-in-water monitors to oil tankers not fitted with segregated ballast tanks. On these ships ballast water is carried in cargo tanks, and the water discharged from the ship is monitored to ensure that the oil content does not exceed an internationally agreed level.

However, it is in the condition and performance monitoring equipment fitted to the motor ship's main engine diesel propulsion plant that the greatest range of monitoring instrumentation is seen.

Oil mist detectors within the crankcase have long been used to detect hot spots caused by localized breakdown of the lubricating film in rotating bearings or between sliding surfaces. Sometimes this equipment is replaced by direct monitoring of the bearing metal temperatures, usually on medium-speed

engine applications. Equally common is temperature sensing of the scavenge air spaces to detect a scavenge space fire. In either of these events an alarm will be raised and usually an automatic engine slow-down initiated.

Traditionally main engine performance monitoring was achieved manually by the taking of 'cards', which were graphs of pressure versus engine rotation obtained from a mechanical indicator, and gave a pressure–volume diagram of the individual cylinder in operation. Many ships are now fitted with the modern equivalent of this equipment. A pressure sensor combined with a rotational pick-up are used to produce the diagram on the screen of an oscilloscope, together with detailed analytical data such as peak pressure, mean indicated pressure, and position relative to TDC, allowing much better understanding of engine performance. The injection fuel pressure is also monitored in a similar way to check injector performance.

Cylinder-head metal temperatures are sometimes monitored to detect thermal overstressing or thermal imbalance of the engine.

The exhaust gas temperature of each cylinder is normally measured. Alarms are raised if the individual cylinder temperature exceeds high or low alarm thresholds and, commonly, if the temperature deviates by a pre-set amount from the weighted average temperature of all other cylinders on that engine.

It is now possible to monitor the condition of the piston rings of each unit in service. Monitors are in use to detect scuffing (micro-welding) of the ring against the liner due to the breakdown of the cylinder lub oil film, and the condition of the rings themselves, whether they are broken, stuck, or operating correctly.

Cylinder liner wear-down sensors have occasionally been fitted with some success to allow detailed evaluation of liner wear at a point during service.

It is common to fit vibration monitoring equipment to all major items of turbo machinery on steamships, and this approach is now being adopted on motorships, with monitoring of vibration levels on main engine turbo blowers, and certain pumps, fans, and alternators.

Currently there are few applications of distributed-control systems or programmable controllers on-board ship. However, a microprocessor-based thermal analyser for steamship plant is in use, which provides data to enable the plant to be adjusted to run at its optimum thermal efficiency.

However, the use of computer-based systems for the dynamic positioning of ships is growing rapidly. It is sometimes the case, particularly in the oil industry sector, that a ship requires to remain on station without the use of anchors. Drilling ships operating in deep water or supply and support vessels required to operate close to production platforms are but two examples. The dynamic positioning system uses various position reference systems to establish its position uniquely. The computer package receives these and other inputs, and controls thrusters, main propellers, and rudders to maintain station in the face of wind, wave, and sea current action.

Computer systems are also in use as load calculators, whereby the stresses, bending moments, and shear force on the ship's hull due to any tank loading configuration can be calculated, as well as for collision avoidance radar and sophisticated auto-pilot systems.

Particular problems exist for the operation of instrumentation in the marine environment, which is typically far more severe than that usually found

onshore. The major differences are the ship's motion, high vibration levels, and high ambient temperatures, together with high humidity and corrosive salt laden environment. This has frequently led to detecting and measuring elements in common use on shore installations proving unsuitable in marine applications.

Special environmental testing procedures are thus laid down by classification societies such as Lloyd's Register of Shipping which requires for instance, that a device shall operate satisfactorily at an inclination of $22\frac{1}{2}^{\circ}$ from the vertical in any direction. Most owners are careful to ensure that all equipment proposed for use in their vessels has successfully passed the tests of one of the classification societies.

The classification societies also provide rules, guidance, and plan approval for systems engineering, and the British Ship Research Association has published a Code of Procedure for Marine Instrumentation and Control Equipment. These documents, class rules, and BSRA guidelines, are widely used in the marine industry.

With the current emphasis on the reduction of costs in all areas of the marine industry there is no doubt that the range and type of automation systems will continue to increase on new shipping, and to be applied to older tonnage on a retro-fit basis.

The prime purpose of control engineering for marine duty should be to improve the accuracy and reliability of the instrumentation fitted, leading to improved operating efficiency of the plant. This must be achieved with simplicity of design and simplified maintenance procedures in order to enable the limited manpower resources to maintain the equipment to achieve its design performance in this complex and challenging environment.

OIL WELLS AND PIPELINES

Those regions of the world where historically crude oil has been found, such as Alaska, the Middle East, and the Niger Delta, have always provided a severe test for instrumentation. The tradition has continued with the harsh environmental conditions in the North Sea, and in other areas where there has also been a swing from onshore to offshore oil wells. While perhaps in the early days of exploration and production in the North Sea the overriding consideration was to get the crude oil flowing and a fairly primitive level of instrumentation sufficed, this has vastly changed. The type and sophistication of the equipment now used equals that to be found in land-based installations, notwithstanding all the difficulties offshore.

At a typical well-head, in addition to the choke valve for production control, there are the sub-surface safety valve, the surface safety valve, and the wing valve for opening and closing the well under normal operating conditions. The operation of the choke valve and the wing valve is interlocked by electronic control equipment to make sure that the sequence of opening and closing is correct. The safety shutdown system includes emergency shut-down, low flowline pressure and high flowline pressure. Emergency shut-down will be automatically initiated by such events as excessive heat. Low flowline pressure could indicate a leak in the flowline and usually closes all well-head control valves, including the downhole safety valve as well as the surface safety valve.

High flowline pressure may be caused by a flowline restriction or downsteam valve closure, and will also close the well-head control valves, although not normally the downhole safety valve. Power supply systems are pneumatic and hydraulic, and both production control and safety shutoff systems tend now to be fully automatic. Production flow rate from each well to the separators can be controlled by using conventional automatic flow control equipment.

The enormous quantity of crude oil being produced at the offshore platforms has to be very carefully and accurately measured, and both metering and proving systems have to comply with the detailed regulations of government authorities. As far as flowmeters are concerned the turbine meter, although originally regarded with some scepticism, is now firmly established on the grounds of accuracy, reliability, and high throughput for the size. Performance data show very little shift in calibration over a period of months, and many meters have been on-stream for up to five years without failure. The accuracy of the meter is dependent upon establishing the K factor for the actual operating conditions, and this is done by making a number of proving runs against a proving loop integrated into the metering system. The proving loop consists of a length of internally coated pipe with an accurately known volume between sphere detector switches, which is swept out by an inflated plastic sphere. To calibrate a turbine meter the pulses from it are counted during the time the sphere is travelling between the two detector switches. Each meter is calibrated against this known volume and is corrected for pressure and temperature to obtain a K factor in pulses per cubic metre of oil. The latest designs of integrated meters and provers, with microprocessor-based electronics for the system display, have proved to be very effective combinations. The aim is to achieve the best possible accuracy, since errors of a fraction of a per cent either way represent very large sums of money. Of course measurement for fiscal, contractual, or loss assessment purposes extends into other areas besides crude oil. Offshore production may involve high pressure gas, liquid natural gas, liquid petroleum gas, and spiked crudes. Many new techniques and methods are being developed for these even wider aspects of flow measurement. The problem may be further complicated by the presence of flow and pressure fluctuations, particularly in high pressure gas.

Another very important requirement is the continuous on-line measurement of density so that volume data can be transferred into mass at the same pressure and temperature conditions. A wide variety of instruments are now available which include the simple buoyancy type, the nucleonic type, and the vibrating element. In the last example the sensing element, which either contains or is immersed in the product, is made to vibrate at its natural frequency. As the density of the product changes so does the total mass of the vibrating system, and hence the resonant frequency. This can be measured, and by suitable calibration provides accurate density measurements. The method is applicable to both liquid and gas, but can be adversely affected by the presence of contaminants such as wax, sand, and gas bubbles in liquid streams. Very accurate calibration standards are needed, and special pressure pyknometers capable of standing up to line conditions have had to be developed.

A major concern is the quantity of water which may be present in the crude oil, and the two measurements—volumes of crude oil and water—have equal

significance in the calculation of dry or net oil quantity. Purchasing contracts have to be drawn up in such a way that the buyer and the seller are mutually satisfied that the water content has been accurately determined. The preferred method at present is automatic sampling which extracts a series of very small quantities of crude oil, known as grabs, as the oil flows along the pipeline. These are collected in a receiver, which is then taken to the laboratory for accurate determination of the water content. Many precautions have to be taken to ensure that the final sample so obtained is fully representative, and these include mixing the flowing stream to make sure it is homogeneous before the grabs are taken. The operation of the sampling mechanism which extracts the ten thousand or more grabs taken from each crude oil parcel or transfer is usually flow proportional, and the pacing signal can be taken from the crude oil flow meters. Of course continuous on-line measurement of water content would offer real time data, and so enable volume measurements for the crude oil to be automatically compensated to provide dry or net figures. However, whilst intensive efforts are being made to develop suitable techniques of continuous measurement there are problems yet to be overcome such as the presence of varying amounts of salt in the water and the difficulty of providing a dry reference sample.

The recent advances in electronic instrumentation have significant advantages when considered for oil platforms and terminals. The increasing use of centralized displays and microprocessor-based instruments and computer systems saves valuable space and provides enhanced operator facilities. Particular attention has to be given to the proper design of panels and consoles, because of the continual turnover and rotation of operators. Thus the layout must provide for an immediate understanding of the monitoring, control, and alarm facilities. Weight considerations, too, are important to avoid overloading the structure. Due to the very long distances between production platforms, terminals, and their coordinating control centres much use is made of various forms of telemetry, such as direct wire, telephone circuits, and particularly radio microwave systems. Incredible amounts of information on production rates, pressures, and temperatures, and the operational state of control valves, pumps and electrical generators can be transmitted by mini-computer based telemetry systems and presented on colour graphic visual display units. This is of tremendous assistance in production control and maintenance analysis.

Another function of mini-computer based telemetry is to provide pipeline integrity systems which by UK law are a mandatory requirement for sub-sea pipelines. A complete visual picture of flows and pressures all along the pipeline gives early warning of major leaks; and line balance calculations, which compare corrected input and output volumes over a period of time, will detect smaller leaks. Another technique of detecting a leak and locating it accurately is based on the decrease in the pipeline fluid pressure in the immediate vicinity of the leak. This sets up a transient pressure wave which is perceived by a sensitive pressure transducer at a remote valve compound.

The safety of production platforms demands automatic and reliable shut-down systems to protect the equipment, the process, the environment, and above all, the personnel engaged in operating and maintaining the facilities.

Highly complex and fully programmable systems are nowadays based on microprocessors, and are triplicated to ensure that a single fault cannot cause a spurious shut-down and waste valuable production time. They respond to sensors detecting excessive pressure, temperatures, levels, flow rates, shaft speeds, and the presence of gas, smoke or flame.

The presence of people on a twenty-four hour basis in the accommodation areas of the production platforms has been recognized by special emphasis on fire detection. The hazard to life arises from burning, poisoning by gases such as carbon monoxide, suffocation, and lack of visibility caused by smoke which may hinder escape. Detection systems vary according to application, so that radiation detectors responsive to infra-red and ultra-violet may be appropriate where flammable liquids or gases are present, smoke detectors for accommodation areas, and heat-sensitive devices as triggers for automatic water sprinklers.

Some hundreds of gas detectors are required to monitor continuously every part of an offshore installation involved in underwater exploration or production, where flammable gas may accidentally accumulate. Much work has gone into developing gas detectors with sufficient weather protection, which are reliable and insensitive to chemical poisoning by sulphur and silicone compounds. Functional testing of all these devices is a necessary but time-consuming affair, especially where they are installed in places where access is difficult. British Standard BS 6020 is now available which specifies the construction, performance, and safety requirements of these combustible gas detectors, and a BSI certification scheme to provide an independent assurance of compliance is being set up.

Pipeline automation has made rapid strides in recent years, and indeed there are now many installations involving transfer of parcels of different, though compatible, products and different crude oils. Thus it is important, especially for common-carrier operation, to measure both quantity and composition in order to distinguish between each shipper's parcel. Determination of the interface is an essential measurement, and may be done by using the meter readings backed up by an interface detector such as a continuous densitometer. Unmanned pump houses and compressor stations along the route have to be monitored with remote valve switching, and automatic start-up and shut-down. Data retrieval systems have been designed to provide bills of lading, invoices, and other commercial transaction documents.

Looking, therefore, at all these new or better techniques of automatic control and instrumentation available today, and comparing them with the situation only a few years ago it is amply clear that there have been widespread advances. Indeed, the pace of engineering development, largely based on micro-electronics, has tended to outstrip the availability of capital resources (and sometimes human resources) to implement all the possibilities. There is much scope and potential for improving the present installations from the borehole to the customer. Without doubt this will take place throughout the industry where it is profitable and economic to do so in the years to come.

RELIABILITY

Now that automatic control systems are so critical for the good performance of the plant careful consideration has to be given to their reliability. The aim is to make the failure rate of the instrumentation insignificant in relation to the failure rate of the plant from other causes. Various techniques are used to achieve this, and as a starting point high-grade components are fitted to electronic equipment and operated at under their design ratings. It is known too, that the failure rate of components is at its highest in the initial stages of their life, and equipment is therefore factory tested for a period under energized conditions before being released for shipment. The failure rate then declines and stays at a more or less constant level during the operational period of around 20 to 25 years, when the equipment reaches the wear-out stage and the rate increases rapidly.

Other factors which influence reliability are the environmental conditions under which equipment has to function, and vibration, dust, and humidity are likely to cause problems. The heat dissipation of large integrated control systems has to be taken into account, and a reliable air-conditioning system in the control room is essential.

Although failure rates are the principal factor in reliability, the instrument down-time influences the availability. The time taken to diagnose the cause of a failure and replace the offending component or circuit board has to be minimal. However, microprocessors are equipped with self-diagnostic programmes, and built-in redundancy with automatic take-over in case of failure.

Refinery plants are run for approximately two years between major inspection and overhaul, and this may be too long for high-integrity safety trip and alarm systems. Hence they should be checked at more frequent intervals, i.e. every three months. It is possible for a fault not to become apparent until the trip has to operate and provide the required emergency action. Of course the principle of 'fail-safe' is to be aimed at, but 'fail to danger' is always a possibility.

Notwithstanding the emphasis on the reliability and availability of the electronic equipment much still depends on the understanding and vigilance of the operator. The final responsibility for the plant rests with him, and in the end he is the last resort. No plant is yet fully automatic in the sense that it completely looks after itself. It may do so for long periods, during which time the operator is relatively inactive, but an unforeseen problem can arise which demands his immediate and direct involvement to restore the plant to its safe condition.

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35

Measurement of Oil, Gas and the Control of Oil Losses

By P. JONES

ACCURATE measurement of oil quantities is of prime importance. Not only does it obviate disputes on receipts into refinery or terminal storage and on deliveries to customers, provide a sound basis for taxation purposes, e.g. on North Sea crude oil and gas production, but it also monitors and helps to eliminate unnecessary product loss. This has become of increasing importance because of the sharp rise in oil prices. To meet all these varied requirements petroleum measurement methods have become increasingly sophisticated and automated.

To measure a quantity of oil it is first necessary to have an accurately calibrated measuring device. This may be the oil storage tank itself, the barge or ship, a road or rail vehicle, or a metering system. While oil stock determination based on direct tank content measurement by tank gauging remains a fundamental and accepted measurement method, still very widely used, for reasons to be outlined there is an increasing trend towards the use of accurate flow metering systems to measure the delivery and receipt of crude oil and products. This is on the grounds of both operational convenience and control, and a necessity, as in the case where crude oil or gas production from a number of offshore fields is transferred through a common pipeline to the shore reception facilities. In certain operational sectors involving the delivery of products measured at ambient temperature, e.g. the retail distribution chain for motor gasoline and heating oils, such volumetric measurement without temperature correction is of sufficient accuracy for all practical purposes. At the scale of other operations, such as the bulk receipt or despatch of crude oil or product cargoes, where reconciliation of bulk quantities in inventory or pipeline transit is to be carried out, and/or where significant variations from the ambient level occur, e.g. as with heated products, temperature correction becomes of vital importance. In these instances it is necessary to measure and record the oil volume, and both its mean temperature and density, in order to correct the volume to standard conditions by applying a volume correction factor (VCF) taken from standard measurement tables relating coefficient of expansion with temperature for the class of petroleum concerned. In the UK, Western Europe, and many countries, the standard reference temperature is 15°C, while in the US the standard remains at 60°F. Thus both metric (15°C) and 60°F sets of tables are published (see later), while for certain countries tables for 20°C are available. The determination of temperature and density also enables conversion to weight or mass.

Tank calibration. Storage tanks and ships' tanks are generally calibrated by calculation based on the dimensions of the tank; for a storage tank these are carefully measured by what is known as the 'strapping' method. In this method

allowance has to be made for obstructions within the tank such as pipework, heating coils, etc. From this procedure it is possible to compile a capacity table giving the volume corresponding to each millimetre of height.

In the case of ships' tanks similar calculations are made, usually based on the shipbuilder's drawings.

Road tanker vehicles are generally calibrated by gradual filling from reference measure containers of known capacity. As each compartment is filled, a rod, known as a dipstick, is marked to give the volume corresponding to the intermediate points, and this rod is then officially numbered and stamped as the calibrated dip rod to be used only in that numbered compartment.

In the case of *rail cars*, since these are generally filled to capacity and the total contents delivered to one recipient, it is usual to 'gauge' each car. This is to say, fill each car to a pre-set reference point and mark the barrel with the total volume needed to reach that point. It is usual nowadays to gauge by filling through meters at the manufacturer's premises.

MEASUREMENT OF RECEIPTS AND DELIVERIES BY GAUGING

To 'gauge' or check the quantity of oil received into storage it is usual to gauge or 'dip' the tank to determine the volume of oil in the tank before and after receipt. Gauging is accomplished by lowering a graduated flexible steel tape, with a weight attached, through the oil until the tank bottom is reached. When withdrawn the level of liquid is clearly discernible on the tape. By relating the depth measurement to the tank calibration tables the volume of oil can be determined. For black products the normal practice is ullaging, that is, measuring the distance from the liquid surface to a reference point at the top of the tank.

If water is present in the bottom of the tank, it can be measured in like manner by smearing the bottom part of the dip tape with water-finding paste. For liquids of a volatile nature a paste is available for making the oil level easier to see.

For economic reasons it is becoming more common to use automatic gauging devices as the means for determining receipt quantities, but these in turn have to be proved and appropriately checked against the method outlined above. The advantage of such automatic devices is that the oil depths can be read from a gauge at the tank side or at a central control point within or even remote from the installation, thus saving time, providing continuous control, and eliminating a great deal of tank top work.

A good tank gauging system can give long-term overall accuracies very comparable to that of a good flow metering system, particularly where large oil movements in or out of the system are concerned, because the difference in gaugings can be measured with much higher relative accuracy than for small ones. However, because of volumetric expansion effects, oil temperature must be measured accurately, which in a very large tank requires considerable care.

Deliveries

It will have been seen from the above that measurement of deliveries from an installation may be accomplished by the use of the gauging method, for

example, when loading a ship at a jetty where there are no loading meters. But for measuring smaller quantities, such as into road tanker vehicles or rail cars, other means are generally more efficient. These quantities are usually determined by filling the tank vehicle through pre-set meters at loading installations and this practice is an important part of the automation of loading gantry procedures. Meters are calibrated against a known standard device which may be a container or another special meter known as a 'reference meter'. It is still important, however, that road and rail vehicles are accurately calibrated, not least because it is the vehicle dipstick measurement or gauged capacity measurement which is available to the customer to check at the discharging location (see chapter on Road and Rail Transport).

Apart from stock measurement there are other areas where tank gauging may be preferred to meter. For instance, turbine meters used for refrigerated LPG have a reduced 'rangeability', and may suffer rapid bearing wear because of its lack of lubricating properties.

Methods laid down for the above procedures are listed under Further Reading. An outline of flow metering is given below.

METER SYSTEMS

(*i*) *Positive displacement type*

The metering of petroleum by a positive displacement (PD) meter is a long established practice, with many types in use. These include reciprocating pistons, rotary pistons, sliding vanes, etc., with tightness of fit against their chamber such that, as their name implies, the number of revolutions (or rotations) caused by the passage of the liquid flowing through the mechanism is an indication of the volume swept by the liquid that has passed. Thus positive displacement type meters are universally employed, for example, in retail dispensing fuel pumps, and almost universally in road tanker loading gantries and similar small to medium size applications where they are used in conjunction with a meter proving system (see below).

The disadvantage of the PD meter is the relatively high weight, and large size, which is several times that of the diameter of the pipe in which it is installed; for the larger flows the more compact 'turbine meter' is now customary.

(*ii*) *Turbine meters*

These consist of a freely spinning rotor, occupying practically the whole of the cross-section of a short machined flow channel of diameter equivalent to that of the adjoining main piping. Turbine meters can be wholly mechanical or may, which is usual, include electrical or electronic components. Thus, inserted in the wall of the flow channel there can be an electromagnetic detector which counts the number of passing rotations of the blades or of the rotor, the number of counts or 'pulses' being related to total volume through the meter. Because of the broader tolerances with such a free rotor, flow slippage will be considerably greater than with a PD meter, and again a meter proving system is utilized to determine by practical means the relationship ('meter factor') between the instrument 'count' and actual flow volume.

Flow straightening elements are provided in the pipework both at the inlet and outlet sides of a turbine meter, and a necessary characteristic of a well designed and selected assembly is good repeatability over the 'rangeability' required, this being the range between the maximum and minimum flow rates for which the meter is intended and between which meter factors will not vary widely or unreliably; this working range will, for liquids in the lower range of viscosity such as light distillate products and most crude oils, usually lie between 5 to 1 and 10 to 1, and it is important that the calibration—or range of meter factors—of the meter is determined by proving procedures at regular and frequent intervals over the full range of flow conditions in which it is employed. These flow conditions will also be affected to a lesser or greater extent by the viscosity of the fluid and variations in its temperature; these factors also have to be taken into account in establishing proving procedures, as when there is a significant change in the physical properties of the flow stream. Where liquids of a higher viscosity than most crudes or distillates are concerned, the restriction in the flow range over which a turbine meter will operate may make the choice of a PD meter preferable. For more details than can be given here, the reviews in 'Modern turbine metering systems for crude oil,' A. T. Hayward, *Petroleum Review,* November 1982, pp. 24–27, and 'Improving turbine meter linearity,' I. Draper, *Petroleum Review,* March 1983, p. 40, can be recommended. Because of its simple design and compactness there is a considerable price advantage between a turbine meter and a PD meter as the size increases (say above 6 in diameter), and the smaller size and weight become of considerable importance when, for instance, installation on an offshore platform is considered.

The Proving of Meter Systems

As outlined above, this is an essential routine operation for either the PD or turbine meter system. Meter provers initially consisted of accurately calibrated volumetric 'prover tanks' into which the flow from the meter system was run for accurate comparison, though cost factors will usually now militate against the use of such a system. An alternative, as used for the checking of the accuracy of flow meter systems at an oil installation loading gantry, is the employment of the 'reference meter' method, in which a reference meter*, previously accurately calibrated, can be used in series with the meter under test to validate the performance of the latter (see Chapter 33).

However, for the reasons given above, the highest accuracy with turbine meters will require provision for re-proving them at frequent intervals (at least weekly for North Sea crude operations) in their installed positions. For this purpose the principle of the 'pipe prover system' has been the optimum, and such a system is built in for every North Sea crude oil metering station. In such a device, a close fitting piston, or more usually an inflated elastic sphere acting as a piston, is swept by the flow along an accurately calibrated length of pipe, at the ends of which are sensitive detectors which emit electrical signals that are used to start and stop the count of pulses from the meter which is being proved. Thus the pulse count from the meter can be compared with the known

* Sometimes referred to as a 'master meter'.

swept volume of the prover pipe between the two detector switch points, with appropriate corrections for temperature and pressure, and an accurate meter factor established.

Pipe provers can be either uni- or bi-directional in operation, the latter (also known as closed-loop systems) employing more complex four-way valving to allow reversal of the flow. The chief advantage of a pipe prover over a tank prover is that during proving the flow of liquid is not interrupted. This permits the meter to be proved under specific operating conditions and at a uniform rate of flow without having to start and stop. Rates can thus be very high if needed. In the earlier days the pipe prover had to be made of large volume, a disadvantage in its use offshore; this has spurred the development of a more compact design and increasingly high precision in the pulse counting procedure. Initial calibration of the volume of a pipe prover is carried out prior to leaving the manufacturer's premises, usually by the direct 'water draw' method. However, there is a requirement in the UK North Sea sector for such provers used for fiscal metering to be recalibrated at yearly intervals, for which such a procedure could not be conveniently employed offshore. A method in which a small master pipe prover, which can be recalibrated onshore and taken to an offshore site and used to recalibrate the main pipe prover has been developed, for an outline of which, and on proving generally, the previously mentioned articles may be read.

Forms of Display with Metering Systems

Both PD and turbine meters may have continuous or discontinuous indication, which may be local at the meter itself, and/or be transmitted to a remote centralized control point. Where such an electric or electronic system is employed, it is necessary to ensure that these elements or systems are effectively isolated from external electrical or electronic influences that could affect the security (i.e. accuracy) of the transmission.

Meters may thus include the following ancillary functions:

Zeroing devices for volume indicators
Totalizing volume counters
Multiple indicating devices
Price computing devices
Print-out devices
Volume or price pre-setting devices.

The sophistication of these options and the large growth in integration of electronic communication linking enables metering systems and associated on-line density measurement systems, etc. to feed in instant data to a centralized computer data processing base, so that the monitoring and documentation print-out of quantity, quality, inventory, distribution, cargo loading, etc. can be carried out. An example is the article 'Counting 1 MBD at Sullum Voe,' *Petroleum Review*, November, 1982, p. 17.

Accuracy of Flow Metering Systems for Fiscal Measurement

It has been stated that the accuracy of a good crude oil metering system is probably of the order of 0.2–0.25 per cent, with probably longer term accuracy

even better because of the elimination of some of the random errors (Smith and Gold; in *Petroleum Review* issue on fiscal measurement, November 1982, pp. 12, 14, 16). These authors, however, make the point in respect of the above assessment that errors in the determination of the water content in a crude oil flow stream must be given consideration, as possibly representing one of the most significant uncertainties in crude oil measurement in terms of 'dry oil basis'.

THE MEASUREMENT OF WATER IN CRUDE OIL

Crude oil in many parts of the world was often from reservoirs from which the production, initially at least, was virtually free from non-oil material such as sediment and water (BS and W), and such small amounts as were present could be neglected. In the case of many reservoirs now on production this is no longer so (see Chapter 6) and, as in the course of shipment by tanker there is also the possibility of the cargo picking up water, it has become necessary to make a further correction of the measured volume in respect of the sediment and water content.

This is not easy since there is no accepted method of on-line measurement, and water contents have to be determined by laboratory tests on samples taken from the pipeline flow. The representivity of such sampling is clearly crucial, because manual spot samples would not be accurate or appropriate in cases where the water may travel as transient slugs. Thus continuous sampling probes are carefully positioned at a point where the oil and water are likely to be thoroughly mixed, with the sample being withdrawn continuously at a rate proportional to the pipeline flow. The procedure is equally applicable in the case of ship/shore transfer where pumping rates can vary widely during discharge. Care has to be taken that the sample withdrawn from the sampler container also remains fully representative, by homogenization before making the laboratory determination; former methods for this include both the centrifuge method for BS and W, and the Dean and Stark extractive distillation method for determining water, but interest in increased accuracy is leading to the direct determination of water by the Karl Fischer method.

The importance of developing good water measurement methods will be apparent in that quantities of the order of 0 to 3 per cent by volume may commonly have to be dealt with. Further reading will be found in Smith and Gold, and on ongoing developments in the article 'Water determination for North Sea crude oils using automatic sampling and other techniques' by W. H. Topham, *Petroleum Review*, November 1982, pp. 28–32.

PETROLEUM MEASUREMENT TABLES FOR VOLUME CORRECTION TO STANDARD REFERENCE TEMPERATURE

Standardization of measurement corrections is essential in such a wide field as bulk petroleum custody transfer, and for this purpose internationally recognized tables have been a key factor. The most widely authoritative of these for many years (and accepted in the International Organization for Standardization under the designation ISO R91) have been the API–ASTM–IP Petroleum Measurement Tables (API 2540; ASTM D 1250; IP 200). A completely updated and revised edition, in both American (60°F) and metric (15°C) units was issued in 1980, replacing the earlier volumes dating back to

1952, except for those sections concerned with density below 0.650 (e.g. LPGs for which the earlier tables remain in use.

The reasons for this revision were: (1) to ensure that the thermal expansion coefficients of current-day crude oils and products in major production and international trading were accurately reflected in the tables, since it was evident that the data on which the earlier tables had been based had become outdated, giving coefficients of expansion that are too small; (2) to reflect the differences between the expansion coefficients of crude oils and those of products, since over a major part of the range of density these are not precisely the same. Thus the 1980 revised edition gives separate sets of tables for crude oils and for products, leading to much greater accuracy in the conversion of volumes measured at temperatures other than the standard reference condition.

The use of the new tables has the greatest impact on volumetric measurements made at temperatures far removed from the reference temperature of 15°C or 60°F. This should result in both (1) reduction in customer complaints in respect of apparent discrepancies, and (2) a more realistic assessment of transit, terminal, and refinery losses.

As an example, the difference between the new and the old tables will apply in the case of crude oils which are usually loaded at fairly high temperature, i.e. generally between 30°C and 40°C, for export from the Middle East. Thus, for a typical crude oil at 35°C, the VCF will be 0.9892 from the revised tables, but would have been read from the old tables as 0.9840, making a difference of 0.11 per cent when the receipts are calculated as compared with the quantities as loaded. Further examples of the use of the new tables are given in IP Technical Paper IP 81–006, New Standard for Volume Correction: Revision of the Petroleum Measurement Tables (IP 200; ASTM D 1250; API 2540), L. Downer and J. R. Spencer.

OIL LOSS MEASUREMENT AND CONTROL

There are many ways in which oil loss can occur. Some are real while others are fictitious. In this last category the most usual is undoubtedly variation in volume with the temperature of the oil. As stated in the preceding section, if oil volume is measured at ambient temperatures when despatched and received, any change of temperature in transit makes it possible to arrive at apparent differences between quantities received and delivered without any oil having been lost. The use of the more accurate volume correction factors of the revised 1980 Petroleum Measurement Tables will give increased accuracy in conversion to standard reference conditions, and so tend to minimize and reconcile apparent but unreal losses.

Real and controllable losses can be broadly divided between those caused by natural processes and those caused by human or mechanical error. Natural losses are due to evaporation, and this type of loss can be placed in two main categories: (i) Breathing losses from tankage; (ii) Displacement or working (filling and emptying) losses. These two categories of loss arise as follows:

Losses from Fixed Roof Tanks

Two significant types of emissions from fixed roof tanks are breathing losses and working losses. *Breathing or standing loss* is the expulsion of vapour from a tank

due to vapour expansion and contraction from daily changes in temperature and barometric pressure. It occurs in the absence of any liquid level change in the tank. The usual means of controlling such losses is by the use of pressure and vacuum valves as described in Chapter 33 in the section on tankage types.

The combined loss from filling and emptying is called working loss. Filling loss is associated with an increase in the liquid level in the tank. Vapours are expelled from the tank when the pressure inside the tank exceeds the P/V valve setting as a result of filling. Emptying or withdrawal loss occurs when air drawn into the tank during liquid removal becomes saturated with vapour and subsequently expands, thus exceeding the relieving capacity of the vapour space and its P/V range of settings.

Data on which to base storage tank evaporation loss calculations have in the past been difficult to obtain, and it has been usual for estimates to rely on API Bulletin 2518 Evaporation Loss from Fixed Roof Tanks, June 1962. Comprehensive studies recently carried out by API in the field have revealed that breathing losses so calculated have been considerably overstated, and API 2518 is to be revised in due course. Pending this, the US EPA based upon API test findings to date has issued its own provisional document 'AP-42, Revised section 4.3 Storage of Organic Liquids, April 1981'. This recommends that for the present, for fixed roof breathing losses the former loss equation in API 2518 be retained, but with the application of the factor of 0.28 to take account of work in this field. Account also should be taken that P/V value settings (see Chapter 33) are considerably wider in range in Europe than in the US, as applicable to the API 650 tank standard under which a pressure–vacuum range of about 6 mbar (+2.5–3.5 cm water) may not be untypical. In contrast, as noted in the IP Refinery Code and Chapter 33, tanks for Class 1 petroleum stocks in the UK can be designed to have a working range of +50 mbar positive to −6 mbar (Δ56 mbar).

A practical survey carried out on evaporation emissions from 127 bulk gasoline storage tanks in the United Kingdom (*Journal of the Institute of Petroleum*, Vol. 41, No. 382, October 1955, pp. 297–325: 'Evaporation Losses from Petroleum Storage Tanks in the United Kingdom—A Practical Survey') showed that breathing emissions became significantly less as the pressure–vacuum relief valve working range increased. Thus taking the data for one particular case it has been estimated that under UK conditions annual standing storage emissions may be reduced by as much as 42 per cent and 86 per cent, respectively, at P/V valve working ranges of 26 and 56 mbar, as compared to the case where a negligible P/V valve working range was assumed.

Losses experienced with fixed roof tankage can be very significantly reduced, by the order of up to 60 to 90 per cent according to the EPA under US conditions, by the use of floating roof tankage for highly volatile liquids. Reductions can also be obtained by fitting a fixed roof tank with an internal floating roof, blanket or cover (see again Chapter 33).

Losses from External Floating Roof Tanks

Standing storage loss, the major element of evaporative loss, results from wind-induced mechanisms as air flows across the top of an external floating roof tank.

These mechanisms may vary, depending upon the types of seals used to close the annular vapour space between the floating roof and the tank wall.

Withdrawal loss is another source of emissions from external floating roof tanks. This loss is the vaporization of liquid that clings to the tank wall and is exposed to the atmosphere when a floating roof is lowered by withdrawal of liquid.

Internal Floating Roof Tanks

Internal floating roof tanks generally have the same sources of emissions as external floating roof tanks. Standing storage and wetting losses are two sources of emissions from these tanks. Fittings losses, from penetrations in the roof by deck fittings, roof column supports, or other openings, can also account for emissions from internal floating roof tanks.

The updated API Bulletin, AP 2517, 2nd edition, February 1980, based on a comprehensive API test evaluation programme can be used for the estimation of losses from external floating roof tankage. Currently API studies to revise Bulletins 2519 and 2523 for internal floating roof tanks are in progress. Meanwhile it should be noted that as defined in API 2519 there is a wide range of such devices available, in which respect factors such as the rigidity of construction (to prevent liquid welling up between joints), the nature of the seal type and fitting, and the effect of apertures through which fittings are mounted, are all relevant to their performance.

In the choice of tankage type and fittings it is important to consider the working conditions of the tank itself, the number of turnovers a year and whether product movement in and out is at a high or low rate, etc., the final selection in most circumstances being by striking a balance between the cost and the expected value of product to be saved. The so-called paint factor is not unimportant in the matter of minimizing evaporation loss from tankage, since white or aluminium finish on the shell and particularly the roof of a tank can minimize solar gain, and thus the expansion of vapours by their rise in temperature, the temperature of the vapour space having been found by the API to be more significant than changes in the tank liquid temperature. Tankage evaporation losses are a complex subject, and perhaps it is desirable that they be put in some perspective. Based on tankage data from European refineries and using the methods outlined in API Bulletins 2518 and 2517, it has been calculated (CONCAWE) that overall hydrocarbon emissions from refinery storage amount to about 0.026 per cent of refinery crude throughput.

There are displacement losses in the filling operations in road, rail, and marine operations, though these are minimized by submerged filling to avoid splash loading. Using the above procedures it has been calculated that the total loss due to loading is 0.037 per cent of the amount of products despatched, or related back to refinery capacity some 0.007 per cent of the crude throughput. Such figures may be overshadowed by the apparent losses calculated by the use, as discussed above, of inappropriate temperature corrections in the stock balance.

To conclude on this theme, losses caused by human or mechanical error are many and varied. Included in these losses are inaccurate calibration of tanks, imprecise measurement, neglect of testing measuring or conservation devices,

overflows and spillages, even dishonesty. The only way to detect and control such deficiencies is through good housekeeping. This means the maintenance of adequate records allowing areas of loss to be identified, combined with good supervision to check procedures designed to counteract mis-use.

Further Reading

Methods are laid down for achieving satisfactory measurement in the Institute of Petroleum's *Petroleum Measurement Manual*. This consists of a number of parts, under these main headings:

Part I	Calculation of Oil Quantities
Part II	Tank Calibration
Part III	Manual Tank Gauging
Part IV	Temperature Measurement Methods excluding Averaging Thermometers
Part V	Automatic Tank Gauging
Part VI	Sampling for Quantitative purposes (Manual and Automatic Pipeline)
Part VII	Density Measurement
Part IX	Codes of Practice for Meters
Part X	Meter Proving
Part XI	Miscellaneous Measurement Tables
Part XII	Static Measurement of Refrigerated Hydrocarbon Liquids
Part XIII	Fidelity and Security of Measurement Data Transmission Systems
Part XIV	Statistical Aspects of Measurement and Sampling.

MEASUREMENT OF GAS

Pressure difference devices (differential pressure flowmeters or orifice meters as they are called), based upon a simple machined hole in a metal plate mounted between two flanges in a pipeline so that it constricts the flow, were developed almost a century ago to use the well-known venturi effect to measure the flow of natural gas in US producing operations by establishing a relationship (the 'flow discharge coefficient' of the meter) between the difference in upstream and downstream pressures at geometrically precisely located tapping points and the mass flow rate in the pipeline. Although still widely used for control purposes to measure the flow of virtually all forms of fluid, the original application of the orifice plate to measure gas flow still occupies a very key position. Whether at the custody transfer/fiscal points for sale or purchase of natural gas from the North Sea in the UK or on the Continent, in the US, or at the delivery stages along the proposed gas pipeline from the Soviet Union to Western Europe, gas measurement will be through orifice meter runs. The reasons for this virtual monopoly for large-scale bulk gas measurement are the simplicity, avoidance of the wear of moving parts in the device, and the confidence that has been built up on the reliability of the well established relationships of orifice flow characteristics whereby performance can be predicted without the need for calibration.

For this reliability the dimensioned aspects of all features of an orifice meter installation have to be very carefully controlled and engineered, among which the ratio of orifice diameter to pipe diameter, machined orifice surface finish, elastic deformation of the plate, pipe roughness and the distribution of the flow approaching the orifice are all important factors of the many that have been explored in numerous reported large-scale testing programmes. These have resulted in the development of an International Standardization Organization standard, ISO 5167:1980 'Measurement of fluid flow by means of orifice plates, nozzles and venturi tubes inserted in circular cross-section conduits running full' as representing the best current consensus of expert opinion in this field. The UK Department of Energy 'Metering Standards for Gaseous Petroleum Measurement' thus specifies ISO 5167 as its requirement for the UK Continental shelf, along with BS 5844 1980, 'Measurement of fluid flow' and ISO 5168:1978 'Estimation of uncertainty of a flow-rate measurement,' although in the US the long-established American Gas Association 'AGA Report No. 3: Orifice metering of natural gas' (New York: Amer. Gas Ass. 1956), continues in use as the recognized American National Standards Institute (ANSI) standard for the measurement of natural gas. A joint ISO committee has, however, been set up (ISO/TC28/SC5–TC30/SC2 Liaison Group) with the aim of reconciling differences, to which end new programmes are being carried out, with coordination and exchange of test facilities across the Atlantic which have been described by one of the co-Chairmen, E. A. Spencer, in 'Progress on international standardization of orifice plates for flow measurement,' *Int. J. Heat & Fluid Flow*, Vol. 3, No. 2, June 1982.

Units of Measurement for Gas

Secondary instrumentation, e.g. line pressure and temperature, pressure differential, flowing density, density at base or reference conditions, must be located so that representative measurements are assured, and as with other metering forms these may be tied into fully electronic computing, totalizing and print-out systems. Hydrocarbon measurements may be in either volumetric or mass units (cubic metres or tonnes); gas is normally measured in volumetric units. All such measurements should be made on single-phase gas, and where volume is the approved measurement it should be referred to the standard reference conditions of 15°C temperature and 1.0132 bar absolute pressure.

For the flow measurement of gases the determination of density is even more critical than in the case of liquid measurement, since the density and the pressure differential are the prime factors from which the flow through an orifice plate is calculated. In the paper 'The application of on-line density meters for fiscal measurement of oil and gas' (*Petroleum Review*, pp. 18–22, November 1982), Stansfield notes that while in most orifice metering stations the density is still calculated from pressure, temperature and gas quality data, this is no longer acceptable on the more critical and large fiscal metering stations, where on-line density meters are now the established devices. His paper describes these instruments, of which one type widely accepted uses a vibrating element (which for gas may be a thin wall cylinder) immersed in the fluid and made to vibrate at its natural frequency; by suitable calibration and

measurement of the change in resonant frequency, accurate density measurement is obtained, stated for liquids typically to be better than 0.1 per cent of the reading, and for gases better than 0.2 per cent. The digital output form of signal from these sensors makes them suitable for modern microprocessor based flow computers.

In many applications the composition of the gas is required, and it is necessary to provide for gas sampling or on-line composition analysis. The measuring system may also be required to report the thermal throughput of a custody transfer stream, which is derived from the addition of calorific value (energy per unit volume) measurement.

Compared to their estimate of 0.2 per cent as a reasonable figure of accuracy for liquid fiscal measurement (e.g. by turbine meter prover systems), and excluding errors in the determination of water content, Smith and Gold suggest for measurement of gas a figure of 1 per cent as probably more typical; the lower accuracy with gas is due to the large compressibility corrections required when metering gas at relatively high pressures and the still inherent uncertainty that has been mentioned for the orifice plate system itself.

For certain gas measurements, BS 4161: Part 6: 1971 'Specification for Gas Meters, Part 6. Rotary displacement and turbine meters for gas pressures up to 100 bar' may be used, again often in conjunction with on-line density meters.

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Road and Rail Transport

By B. L. VEALE

DISTRIBUTION

Primary, Secondary, and Direct Movements

The movement of oil products from the refineries to the consumer is in general carried out in two stages. The first movement, known as primary transport, is from refineries to terminals, whilst the secondary transport moves the oil products from terminals to customers. Direct deliveries are also made from refineries to customers where appropriate to the type of product supplied.

Whilst rail transport plays an important part in primary transport, its contribution to secondary transport is much smaller, with road transport predominating. In the case of direct deliveries both road and rail transport play a significant role.

The choice of the mode of transport, whether road or rail, water or pipeline, is not made on the grounds of transport costs alone; decisions as to the mode of transport are made in the context of total distribution costs.

Total Distribution

Transport cannot be considered in isolation, but must be recognized as a sector, albeit the most important one in terms of cost, of the total distribution. Total distribution covers the three modes of transport, primary, secondary, and direct, together with the storage and handling of all oil products at refineries and terminals.

The objective is to achieve the lowest total distribution costs for the total movements of all oil products. From this it follows that minimizing any one type of cost, e.g. secondary transport costs, will not necessarily be the right policy in relation to the minimization of total distribution costs.

Proportions Carried by the Various Modes of Transport

The proportions of oil product movements carried out by each mode of transport differ for the two stages of movement. These proportions have changed in recent years and are still changing. As a general principle, the larger the bulk batch transported, the lower the unit transport cost, and as a result movement of oil products in the first stage, together with the direct deliveries, is carried out using the largest feasible batches.

In the second stage, the bulk transported is largely dictated by customers' requirements and facilities for storage, and thus the volumes are much less, in the main, than those obtaining in the first stage.

Hence rail transport is mostly concerned with the primary stage, with road transport mainly handling the second stage. In the case of direct deliveries from refineries both road and rail are involved.

Intermediate Storage—Terminals

Where customers are situated within an economic road radius of a refinery, direct deliveries can be made. Similarly those customers who can be supplied economically by rail, water, or pipeline can receive direct deliveries from a refinery.

Where these conditions do not apply customers must be supplied through an intermediate storage facility, i.e. a terminal. The number and location of terminals are determined by the need to achieve minimum total distribution costs, in accordance with the two principles of minimizing handling and maximizing the volume delivered. The use of intermediate terminals assists in meeting the fluctuating demands for many products, not matched by refinery output, by holding adequate stocks of the range of products to be delivered from the terminal to meet customer demand.

The need for terminals as intermediate storage, and primary and secondary distribution will now be clear. Terminals must be large enough to obtain economy of scale in respect of the storage facilities, near large centres of consumption which will help minimize secondary transport movements, and be capable of being supplied economically from the refinery. This requires the terminals to be supplied with the largest feasible quantities of the range of products stored.

Direct Deliveries—Economic Road Radius

Customers within the economic road radius of a refinery are those who are situated where direct deliveries by road can be made more economically than by any other mode of transport. A great number of customers do lie within the economic radius of refineries, and consequently refineries have associated road delivery terminals generally sited adjacent to the refinery, and from these terminals operate the larger fleets of vehicles. Whilst a normal terminal might have a fleet of from 15 to 50 vehicles, refinery terminals may well have a fleet two or three times larger.

Beyond the economic road radius from the refineries the choice of direct supply to customers lies between rail, water, and pipeline.

Secondary Transport—Road

As previously stated, road transport dominates the secondary transport scene, due to the fact that the principal constraint on secondary transport is the customer's storage capacity. Unless this capacity exceeds 100 tons minimum it is unlikely that deliveries of oil products will be made by rail, water, or pipeline, and the smaller the customer's storage capacity the more certain it becomes that deliveries will be by road transport.

Customers with large storage capacities are likely to be supplied direct from refineries; as a result secondary transport is predominantly road transport.

Legislative Effects

In many centres the total distribution concept is well established with regard to movements of oil products. The variations which exist in national

environments can cause great differences in the proportions of products moved by road and rail. One factor in the environment is the legislative one; and whilst this alone cannot greatly influence the mode of transport for particular movements, the ultimate aim of some legislation can well be to change modes of delivery. As an example, from time to time efforts are made to force road traffic on to rail, usually by raising the level of taxation on road vehicles operating beyond a certain distance from base.

However, because of variations in legislative conditions, together with geographical differences, it would be unwise to generalize about road and rail transport of oil products. Therefore this chapter will be concerned with road and rail transport as it is today, and as it is expected to develop within the UK.

ECONOMIC CRITERIA

It can clearly be seen that whatever mode of transport is considered, the most economic rate will be obtained from the use of the largest capacity units. Physical and legal constraints will automatically set limits for each mode.

Developments in both road and rail vehicles have given opportunities in recent years to increase the size of vehicles. Table I shows what effect these changes have had on vehicle capacities in both modes.

TABLE I

Mode of transport	Year						
	1950	1954	1957	1962	1964	1970	1983
Rail (tons)	20	—	22	27	32	65/74	
Road (litres)	16 300	18 100	—	—	22 600	30 000	36 000
Maximum compartment capacity							
Road (litres)	2 730	3 630				5 000	7 600

Table II shows the total amount of oil products moved, by mode, in 1981.

The increasing use of larger and more expensive transport units has brought in its train an intensification in the quest for better utilization of such units. Idle time must be reduced to the minimum, if not eliminated entirely, and conversely working time extended to approach twenty-four hours a day as closely as is practicable.

The most efficient use of the working time and the transport unit itself must be realized and this necessitates a closely monitored control system.

In the case of block trains, for example, where loads up to 1600 tons gross (1630 tonnes) are moved at speeds up to 60 mph (97 kph), it is clearly vital to control and minimize the turn-round time of these trains at terminals. For road vehicles, capacity utilization, in which the drop size is important, the degree of double and treble shifting of vehicles, the mileage run and the time taken by vehicles making given deliveries, in which the routing and scheduling of the vehicles play the major role, the delivery system itself—these are the principal factors that decide the efficiency of a road transport fleet. They will be dealt with later in the section on road transport, but it will be evident that, for road

TABLE II
Total Movements of Oil Products (All Companies, UK)—1981

Mode of transport	Millions of tons	%
Road	64	32
Rail	12	6
Inland waterways	1	—
Coastal shipping	50	25
Pipeline	75	37

vehicles, it is the vehicle–driver combination that is really the subject, and that consequently all actions intended to increase vehicle utilization and efficiency are in fact dependent on the full and active co-operation of the driver. Hence the productivity agreements with the drivers' unions without which control of large vehicle fleets would be impracticable.

ROAD TRANSPORT

UK legislation covering the design and construction of road vehicles conveying dangerous substances is the responsibility of two Government departments, the Department of Transport and the Health and Safety Executive.

The Department of Transport is concerned with the construction and use of road vehicles, whilst the Health and Safety Executive deals with the conveyance of dangerous substances, and included in this category are low flash point petroleum products such as LPG and motor spirit, also products with flash points up to 55 °C, as well as hot products like bitumen.

Reference to Table I will show how the capacity of road tank vehicles carrying low flash point petroleum products has increased since 1950. The maximum vehicle capacity was restricted to 16 370 litres, with a maximum compartment capacity of 2730 litres. By 1964 the gross laden weight of large articulated vehicles had been increased to 32 500 kg on four axles, but the volume of low flash point products permitted to be carried at this gross weight was not allowed to increase until 1966. At that time the maximum capacity permitted for low flash point products, i.e. petroleum spirit, was raised to 30 000 litres, with a compartment capacity of 5000 litres.

Following the publication of the Armitage Report which recommended increased gross vehicle weights, the UK limit was raised on 1 May 1983 from 32 500 kg on four axles to 38 000 kg on five axles. The choice of axle configuration under this legislation is left to the user, the options being a 4 × 2 tractive unit with tri-axle trailer or a 6 × 2 or 6 × 4 tractive unit with tandem axle trailer.

Fleet Size Policy

As previously stated, secondary transport delivering oil products from terminals to customers is dominated by road transport. Customer demand is, however, not uniform throughout the year, and whilst the seasonal peak

demands of some products balance to some extent troughs in usage of other products, the optimum fleet size of a company engaged in marketing oil is usually a compromise; a compromise between a fleet fully capable of satisfying maximum demand, which means idle vehicles and drivers in periods of low demand, and a fleet which is capable of satisfying only the minimum demand, which in turn means a high level of dependence on hired vehicles.

Clearly vehicles cannot be considered in isolation from their drivers. To ensure the most efficient use of the large capital asset represented by the road vehicle fleet, the fullest co-operation and collaboration with the drivers is essential. In this respect it is important that idle time is eliminated and productivity improved over the whole vehicle fleet: These objectives are met by the introduction of productivity agreements with the drivers' unions.

Changes in Road Vehicle Design

Road vehicle design within the petroleum distribution industry has seen considerable changes over the last 20 years, and with these changes have come the increased safety of vehicles and increased operational efficiency.

Legislation affecting the design of road tank vehicles has moved forward steadily, and progress is maintained by constant dialogue between the Health and Safety Executive and the Institute of Petroleum's Panel 'C'.

Probably the most significant step forward in the period has been the introduction and the almost universal use of light alloy tanks. Light alloy tanks were first introduced around 1960, and whilst originally their cross-section followed the elliptical form favoured for many years for steel tanks, the 'Max' section has become the standard section used for the majority of road petroleum tankers (Fig. 1). Basically 'Max' section ends were designed for tankers which do not operate with pressure discharge and where height and length restrictions did not leave sufficient space for the required volume of product

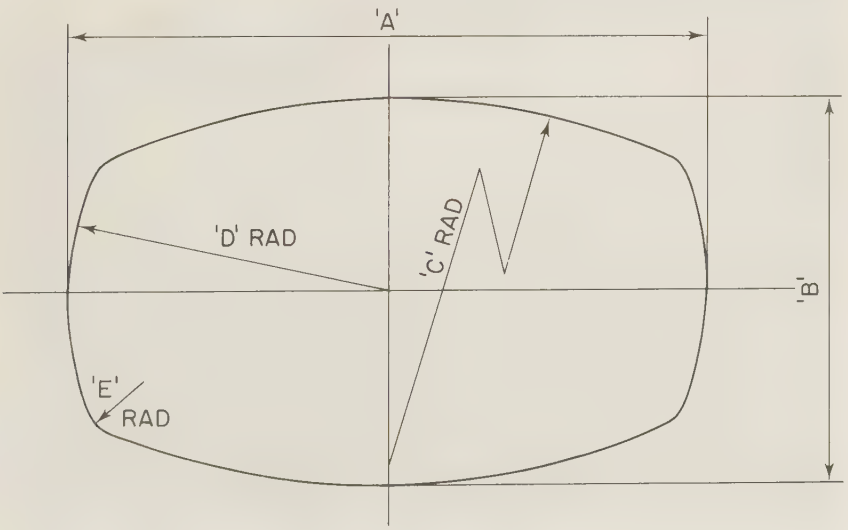

Fig. 1.

FIG. 2. A typical 32.5-tonne tank trailer vehicle.

FIG. 3. A GRP tank trailer vehicle.

to be carried using the conventional type of section, i.e. round or elliptical, favoured for many years for steel tanks. Naturally, as the bottom, side and top radii are increased the section becomes less rigid, and a general loss of strength takes place.

Most tanker manufacturers have stressed out their 'Max' section, and have arrived at their own values for the C, D and E radii, taking consideration of the type and thickness of material, weld distortion, method of mounting support, etc. Obviously the A and B dimensions (width and depth of section) are adjusted to suit the chassis width and vehicle maximum height.

The advent of the 38-tonne vehicle, which has to be constructed with an overall length of 15.5 m, means that the 'Max' section will be the form suitable for aluminium or steel tanks. This comes about because a tank with this form has a greater carrying capacity per centimetre of length than an elliptical tank having the same major and minor axes. As an example, in a typical 32.5-tonne articulated tank, at its deepest section the 'Max' section will hold 36 litres per centimetre run of tank, whereas the corresponding elliptical section will be able to hold only 33.6 litres per centimetre run, an improvement of $7\frac{1}{2}$ per cent in capacity for a given length.

As a result of the changes in legislation referred to and the need to employ the largest vehicle consistent with delivery restraints, to reduce delivery costs the mix of most vehicle fleets is made up of both rigid and articulated vehicles of varying capacities.

The aim at all times is to increase the carrying capacity of the individual vehicle fleets operating at terminals, and this policy has seen major reductions in vehicles of the 16–24-ton weight range, with the emphasis now being placed on large rigids of 30-ton gross and on large articulated vehicles of 32.5-tonne and shortly 38-tonne gross weight.

Another change in road vehicle fleets in recent years has been the greater degree of standardization achieved by reducing the number of individual chassis makes and types operated to the minimum, and also by standardizing on tank designs, layouts, and capacities. The achievement of a high degree of road vehicle fleet standardization has removed many of the problems experienced in the past. Mention must be made of the recent introduction of petroleum tanks constructed in glass-reinforced plastics (GRP). Tanks in GRP can either be of filament wound construction with the glass fibre filaments being formed over a mould, or can be of individual cell construction where the inner cells are formed from fibre-reinforced chemically-resistant resin, and the cells are then positioned inside a fibre-reinforced polyester resin nacelle and retained in position and separated from each other by fire-resistant polyurethane foam. The section of the tank in this instance is rectangular.

Figure 2 shows a typical 32.5-tonne 'Max' section tank trailer vehicle constructed in aluminium alloy with rubber suspension, the tractor being a Seddon Atkinson. Figure 3 shows a GRP tank trailer vehicle designed to operate at 32.5 tonnes.

Technical Developments in Vehicle Design

With the need to maximize payloads and reduce vehicle unladen weight there has been significant progress in recent years in the development of lighter,

reliable vehicles. Early efforts at weight reduction, whilst meeting weight criteria, had a tendency to be less reliable and to suffer more structural failures than their heavier counterparts. Over the past five years there has been progressive weight reduction of both chassis and tanks without any reduction in quality or reliability.

In the case of the chassis, both rigid and tractor models, aluminium components have been introduced in a number of areas. Wheels, fuel tanks, bumpers and even cross-members are now made in aluminium with significant weight reduction.

Currently one engine manufacturer is introducing a 10-litre turbocharged diesel engine which will eventually be offered with power outputs of up to 330 bhp, a rating considered necessary by some users to power the new generation of high performance 38-tonne vehicles. By careful redesigning the engine and its associated equipment weigh some 250 kg less than previous models developing power in this range.

Gear-boxes are now available with aluminium casings, giving a weight reduction of some 50 kg.

On rigid vehicles the use of rubber suspension of the rear axle(s), in addition to reducing chassis weight by 100 kg or more, eliminates spring breakage and gives better road performance in terms of traction and braking.

Considerable attention is being given to achieving weight reduction throughout the chassis without in any way reducing the reliability of the vehicle, and manufacturers' efforts are still continuing in this field. With the increasing use of aluminium and composite materials it is reasonable to expect further weight reductions of from 250 to 500 kg on a chassis over the next few years.

The opportunities for weight reduction on trailer tanks are less than for chassis, because most trailers are already constructed in aluminium alloy with only the minimum of steel components. One clear area of weight saving on trailer tanks concerns the wheels and tyres. The use of the low-profile large single tyre and wheel has been common with a number of petroleum distribution fleets for some years, and these wheels and tyres can save up to 200 kg of unladen weight, with the added bonus of improved fuel performance due to reduced rolling resistance.

Braking performance has improved to match increased engine power and high road speeds, and often the basic braking system is complemented by engine exhaust brakes or retarders incorporated in the transmission.

The manual gear-box is still the most popular transmission used in petroleum fleets, but some users are investigating the use of semi- or fully-automatic transmissions in order to assist in vehicle road performance in urban areas where traffic is heavy.

Influence of Road Vehicle Changes on Costs

Considering the change in unit costs that results from the use of a larger capacity vehicle, it will be understood that the more efficient the utilization of the larger vehicle, the greater will be the improvement.

Clearly the larger vehicle is more expensive than the smaller, and hence the standing cost per hour is higher. The running costs per mile will also rise a

little, so the cost of a trip, in which the full load of the vehicle is delivered to a consumer, will be higher for the larger vehicle. However, the larger the carrying capacity of the vehicles, the less will be the unit cost per litre delivered. It follows, therefore, that maximum capacity vehicles must be used wherever possible to reduce unit costs.

It will be appreciated that costs such as these can only be calculated with accurate knowledge of trip times and routes, i.e. of such items as:

(i) Loading and discharge times of the vehicle;
(ii) Administration times of the vehicle at terminal and consumer;
(iii) Average speed on the road, or, preferably, standard times for specified routes;
(iv) Use of vehicle—single or double shifted.

It follows that any change in vehicle design, construction, or operation and any change in terminal facilities that affect any of these items thereby affect the unit delivery cost of that vehicle.

Vehicle Utilization

Effect of drop size

The largest number of maximum capacity road tank vehicles currently in use are of 30 000-litre capacity, but with the introduction of the 38-tonne vehicle with its practical capacity of some 34 000 litres at present, unit costs will be reduced.

The maximum benefit that could be realized from their use would arise if the vehicle always made single drops equal to the carrying capacity. This state of affairs could only arise if consumers' tankage could somehow be increased overnight to accommodate this single, large drop, and such an increase is a long-term proposition.

However, the principle of increasing the size of drop is a short-term proposition which has a marked effect upon delivery costs, because it will permit a reduction in calls to consumers, whilst maintaining the same high quality service, and this offers opportunities to reduce the number of vehicles making deliveries.

Clearly the larger vehicle offers the greater possibility of increasing average drop sizes, even if consumers' tankage remains unaltered, and hence it may be expected that drop sizes will increase substantially in the next decade.

Routing and scheduling road vehicles

A proportion of vehicles make single drops; most vehicles make two or more drops on a single trip or route, i.e. they are routed to make multi-drop trips. The process of relating all the orders for a given day to the vehicles available on that day, so that all the vehicles are utilized as efficiently as possible, involves first making up the routes of the vehicles and then allocating routes to vehicles in accordance with the shift pattern.

Utilizing vehicles efficiently means that the optimum combination of maximum use of capacity, minimum distance travelled and maximum working

time per shift, is required. Such planning has hitherto fallen to despatch clerks, but the steady increase in the work-load and the search for reducing transport cost, which are obviously directly connected to the number and distance of trips made by the vehicles, has led to the investigation of routing and scheduling by computer. Several commercial computer programs are available which will construct routes on a mileage minimization basis, and the use of such programs has indicated that manual routing can be substantially assisted and hence operating costs reduced.

It is considered that computerized routing and scheduling of vehicles are likely to offer greater benefits where the operations are large-scale; the delivery system can be planned or unplanned. Small-scale operations, involving five to ten or even twenty vehicles, could be assisted by the intermittent use of a computer. Large-scale operations are likely to benefit because savings in mileage should lead to savings in time and hence in vehicles; the latter alone can provide sufficient cost savings to justify the initial data collection work and installation of data transmission links between terminals and computer centre. Currently a number of aspects of vehicle operations and the associated documentation are being linked into operators' computer networks.

Shift patterns

A vehicle used on single shift can be operated for six shifts per week, whilst the same vehicle worked on a double shift basis can work eleven shifts a week. The rate at which a vehicle works during the week will depend on the hours available in the driver's shift.

Drivers' daily hours at the wheel are restricted to a maximum of eight hours. The pattern of drivers' permitted spells at the wheel is laid down in EEC Regulation 543/69 as amended, and the Transport Act 1968 covers operations within the UK for drivers of goods vehicles exceeding 3.5 tonnes gross plated weight, including any trailer drawn by the vehicle.

Petroleum products carrying vehicles are expensive assets, and it is essential that maximum use is made of the vehicles, and therefore double or even in some circumstances treble shifting will be necessary.

The increased annual mileages brought about by greater work-loads has the effect of increasing the work-load in maintenance and repair, and the multi-driver use of vehicles has removed the one vehicle one driver relationship; as a consequence vehicle down-time has increased further as vehicles no longer benefit from a high degree of personal care and attention.

Productivity agreements

As stated previously, and as is self-evident, a vehicle must be considered as a vehicle–driver unit. Reduction in vehicle operation costs that result from the improved utilization of the vehicle clearly depends on the driver. For example, more productive hours worked by the vehicle can only arise if drivers are willing to operate a multi-shift pattern of work. Again, more efficient use of vehicles will result if standard trip times are established, thus permitting accurate scheduling. Both these examples illustrate features that have been

negotiated with drivers through their unions, and incorporated in productivity agreements. Such agreements will obviously continue to play a prominent part in road vehicle operations, since most increases in efficiency must result from the better use of the vehicle plus driver combination, not just the vehicle alone.

Legislation

Whilst it is not possible here to cover details of road vehicle legislation, it is of interest to look at recent changes that have an effect specifically on vehicles used to convey petroleum products.

Increases in permitted vehicle maximum gross weights will allow extra payload of up to 25 per cent on the largest articulated vehicles and it is expected that, although gradual owing to customer acceptance and vehicle provision, this will result in fewer vehicles to deliver the same amount of product. Associated with this change is the requirement for side-guards and rear under-run protection.

The Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981 caused the industry to take a fresh look at the detail of operating vehicles. Included in these regulations are new or revised requirements as to hazard warning panels, information in writing to be available during conveyance, driver training, tank construction, the last item being covered by an Institute of Petroleum Code of Practice. (IP Road Tank Vehicle Design Notes.)

The requirement to have tanks calibrated by Trading Standards calibration centres called for by The Measuring Equipment (Liquid Fuel delivered from Road Tankers) Regulations 1979 has caused some concern about vehicles constructed before that date. These vehicles were not designed to comply with the latest regulations, and the industry is having to deal with the problems created by further consultation with the Department of Trade in order to enable older tank vehicles to be kept in service without the need for extensive modifications.

The need to retain current vehicles in service after modification to enable them to operate at higher gross weights will require compliance with new legislation. The provision of side and rear under-run protection on vehicles operating at gross weights in excess of 32.5 tonnes requires consideration.

Where trailers are liable to be connected to tractors plated to operate in excess of 32.5 tonnes side and rear under-run protection will have to be fitted and maintained at all times, in order not to break the law when operating at the higher weights.

Apart from the loss of payload, estimated at some 150 kg, there is a legal obligation to maintain this equipment in working order at all times.

All new vehicles with a maximum gross weight exceeding 3.5 tonnes and which are manufactured on or after 1 October 1983 and first used on or after 1 April 1984, and trailers with an unladen weight exceeding 1020 kg manufactured on or after 1 May 1983 will have to be fitted with side and rear under-run protection.

The detailed layout of side-guards as laid down in Statutory Instrument 1982 No. 1576, The Motor Vehicles (Construction and Use) (Amendment) (No. 7) Regulations 1982 and in Statutory Instrument 1983 No. 471, The

Motor Vehicles (Construction and Use) (Amendment) (No. 2) Regulation 1983, applies only so far as is practicable in the case of a vehicle designed solely for the carriage of a fluid substance in a closed tank which is permanently fitted to the vehicle and provided with valves and hose or pipe connections for loading or unloading.

The design and construction of road tankers used to convey flammable liquids for pump or gravity discharge is covered by an Approved Code of Practice currently being finalized between the Institute of Petroleum and the Health and Safety Executive.

All aspects of design and construction of chassis and tanks, including the alternative tank shell materials, are covered in the Approved Code of Practice. Copies of the Code are available from the Institute of Petroleum. Vehicles constructed to the Code will satisfy all legal requirements within the UK.

RAIL TRANSPORT

Categories of Rail Tank Cars

All rail tank cars are constructed in accordance with the regulations of the railway authorities, and in the United Kingdom they fall into the following main categories:

(1) Those designed to carry motor spirit and other like products flashing below 73°F (22.8°C). (Note: British Rail has now adopted the same division point of 21°C flash point as is used in present UK legislation. See Chapter 32.)
(2) Those built to carry middle distillates and unheated fuel oil.
(3) Those fitted with steam coils for carrying heated fuel oils. These cars are lagged as well as coiled.
(4) Those for carrying bitumen, which are fitted with flame tubes in addition to having steam coils and lagging.
(5) Those built specially to carry liquefied petroleum gases such as propane and butane. The barrels of these vehicles are of special construction to withstand high pressures.

Loading

The loading of rail tank cars is chiefly carried out through the manholes on the top of the vehicle, and the latest equipment is fully automated. Loading rates of up to 250 tons (254 tonnes) per hour are achieved by this method, and a bogie vehicle can be loaded in 12 minutes through two manholes.

The filling cycle with this equipment is briefly as follows. The rake of tank cars to be loaded is brought to the filling area by the locomotive. Winch-driven 'mules' then take over and the rake is moved progressively car by car through the loading gantry. The final positioning under the loading lances is carried out by the operators on the gantry platform. Once the lances are lowered into the tank cars, control is passed to the control room and the loading is under their direction. Each hydraulically operated loading lance is telescopic, generally 6 inches (152.4 mm) in diameter, and has a flow rate of 250 tons (254 tonnes)

per hour. The lance carriage has a horizontal travel along this overhead track of around 6 ft (1.8 m) and the vertical travel is 10 ft (3.05 m).

For each loading operation the following data are set on the console in the control room and can be checked visually by the operators:

(1) Grade of product to be loaded.
(2) Whether product is duty-paid, under bond, or duty-free.
(3) The railcar number.
(4) The quantity to be loaded in gallons at loading temperature.
(5) The customer's code number.
(6) The code number of the train.

After the required quantity has been delivered into the railcar, the lance withdraws automatically at a set timing. The information previously set is recorded in the memory drum of the computer and is printed out in document form as required.

Another method of top loading is by means of loading arms set at predetermined distances on a raised gantry, and usually preset meters are used.

The rake of tank cars to be loaded is positioned by the locomotive alongside the loading gantry and a loading arm is placed in each manhole as near the bottom of the car as possible to avoid splash loading. Upon completion of loading, the manhole covers are closed and properly secured before the vehicles are removed from the gantry.

Some oil companies fill their vehicles through the bottom, in which case a self-sealing coupling has to be used, and a device for cutting off the flow of the product should be fitted inside the tank.

Discharging

All products can now be discharged through the bottom outlets, although until the 1960s motor spirit had, by regulations, to be discharged overhead via suction pipes.

The modern vehicle has the following discharge fittings:

(1) A main central foot valve in the bottom of the tank, operated from ground level by a lever system from either side of the vehicle.
(2) Secondary outlet valves, one each side of the double-arm outlet tee-piece.
(3) On each side of the outlet pipes either a quick-acting coupling with a sealing cap or a self-sealing coupling with dust cap.

Spring-loaded cam-operated foot valves with special seatings manufactured from materials to suit the commodity to be carried, full-bore ball valves with stainless steel, non-ferrous or plastic-coated ball plugs, and quick-acting couplings now form part of the standard discharge equipment on modern rail tank cars.

Dimensions

Typical 45-ton (45.7-tonne and 100-ton (101.6-tonne) GLW vehicle (as shown in Figs 4 and 5) dimensions are given in Table III.

FIG. 4. A 45-ton GLW rail tank car.

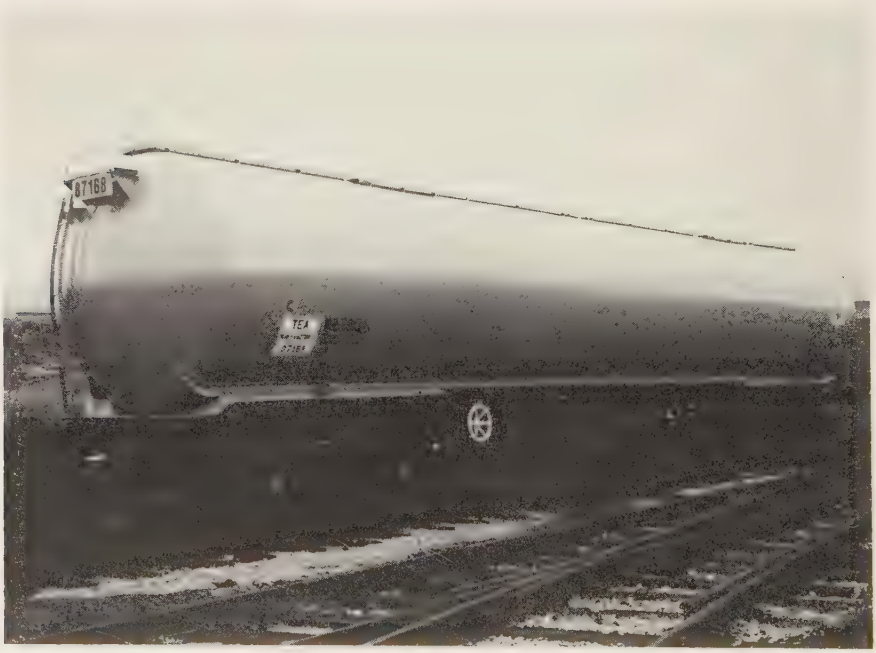

FIG. 5. A 100-ton GLW rail tank car.

TABLE III

Typical Dimensions for 45-ton (45.722-tonne) and 100-ton (101.605-tonne) GLW Vehicles

Description	45-ton GLW		100-ton GLW	
Overall length	29 ft 1 in	8.865 m	58 ft 3 in	17.755 m
Length over head stocks	25 ft 8 in	7.823 m	54 ft 10 in	16.713 m
Rigid wheelbase	15 ft 0 in	4.572 m	—	—
Bogie wheelbase	—	—	6 ft $6\frac{3}{4}$ in	2.00 m
Centres of bogies	—	—	41 ft 9 in	12.725 m
Buffer height	3 ft $5\frac{3}{4}$ in	1.06 m	3 ft $5\frac{3}{4}$ in	1.06 m
Overall height	13 ft 0 in	3.96 m	13 ft 1 in	3.988 m
Outside diameter of barrel	8 ft 9 in	2.667 m	8 ft 9 in	2.667 m
Overall length of barrel	24 ft 6 in	7.468 m	55 ft $8\frac{1}{2}$ in	16.980 m

Carrying Capacity

The carrying capacity of rail tank cars is governed by three things:

(1) The maximum gross laden weight (GLW) permitted by British Rail.
(2) The British Rail W5 loading gauge.
(3) The air space allowed for the expansion of the liquid carried.

Axle loadings of $22\frac{1}{2}$ tons (22.9 tonnes) are the norm in the United Kingdom, but there are also many routes available for the heavier bogie tank wagons with 25-ton (25.4-tonne) axle load, which is the maximum permitted on British Rail lines.

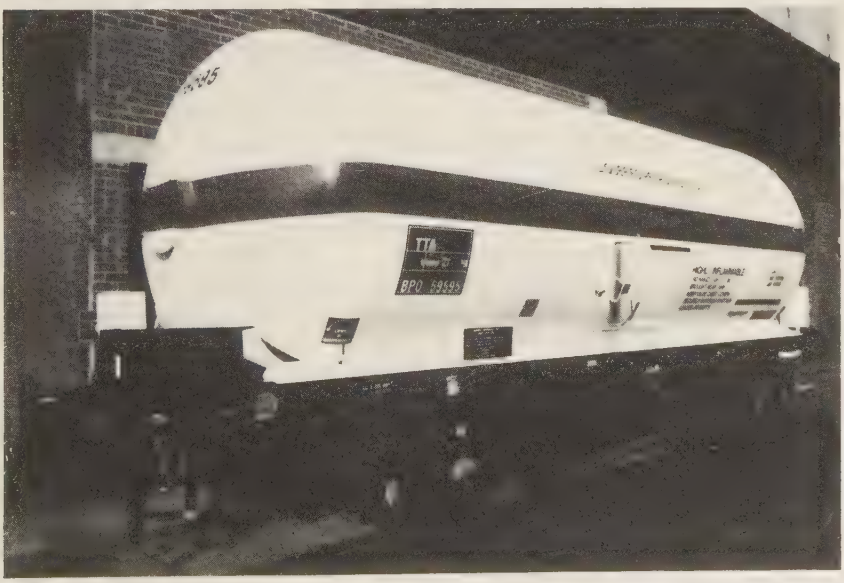

FIG. 6. A rail tank car to carry liquefied petroleum gases.

The permitted overall height of vehicles on British Rail is 13 ft 1 in (3.988 m) and the overall width on the centre line of the barrel is 9 ft (2.743 m).

The air space allowance laid down by British Rail is as follows:

Motor spirit	$3\frac{1}{2}\%$
Fuel oils	2%
Bitumen	$1\frac{1}{2}\%$

The largest modern vehicle is the 100-ton (101.6-tonne) gross laden weight bogie tank car, which has a net capacity of over 19 500 gallons (88 650 litres), giving a payload in motor spirit of 65 tons (66.04 tonnes) and 74 tons (75.19 tonnes) of fuel oil. Most two-axled vehicles at present in service have a capacity of 8400 gallons (38 190 litres), giving a payload of $27\frac{3}{4}$ tons (28.20 tonnes) motor spirit and 32 tons (32.5 tonnes) fuel oil. Some two-axled vehicles of 50 tons gross laden weight are in use and these have a payload of around $36\frac{1}{2}$ tons of heavy fuel oil.

Rail tank cars carrying motor spirit are painted dove grey and the two main members of the underframe, i.e. the solebars, are painted red for identification purposes. Rail tank cars carrying petroleum products flashing above 73°F (22.8°C) are usually painted black. The barrels of those carrying liquefied petroleum gases are painted white and have an orange band, 30 cm wide, around the centre of the barrel longitudinally in accordance with Continental practice. Figure 6 shows a rail tank car to carry liquefied petroleum gases.

Repair and Maintenance

All tank cars running on the main lines of British Rail are regularly inspected, lubricated, and maintained, and every six or seven years they have a complete overhaul, being passed for service by railway inspectors. All vehicles are power braked and the systems are overhauled every three and a half years, although the trend is now to have an annual air brake test instead. The barrels on tank cars for carrying liquefied petroleum gases are tested every six years.

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Health and Hygiene in the Petroleum Industry and in the Processing and Use of Its Products

By P. JONES

An important and ever increasing active concern in all industries is the study of both occupational health and the health, safety, and toxicological aspects of the materials that they handle, process, and place on the market. Today, legislation in practically every country (e.g. the Health and Safety at Work Act 1974 in the UK) places the responsibility for these duties on the manufacturer, supplier, importer, and distributor, and it is important that adequate information is made available to those who are users, whether as employees or the general public, so that both warning as to hazards or misuse, and correct precautionary measures are fully understood and if necessary strengthened.

For hydrocarbon solvents this subject has been dealt with in Chapter 25. This chapter deals with the subject on a wider basis.

TOXICITY

Toxicity is the capacity of a material to produce injury if it reaches a susceptible site or sites on or within the body. Toxic effects may either be acute (e.g. H_2S) or chronic (e.g. the effects of prolonged exposure to a carcinogenic chemical or unrefined mineral oil). A substance is said to be 'acutely toxic' if it produces effects within a short period of time following exposure, and 'chronically toxic' if effects result only after prolonged or repeated exposures measured in days, weeks, months, or even longer. In some cases, an example is exposure to asbestos fibre, there may be a latent period of many years before the effects appear.

The petroleum industry has long been active in investigating the health hazards that may arise in the processing of oil and the handling of its products, and ensuring that the means for adequate protection are promulgated. In the course of this short chapter it is possible to make only a brief incursion into this subject, but some of the basic factors will be touched upon.

It has been stated that 'no substance is wholly safe; there are only safe methods which can be devised to handle them'. This is true of many, if not most materials that are in everyday use. Much of the attention of the petroleum industry has been concerned with the potential carcinogenicity of certain mineral oil fractions and the formulation of the appropriate refining treatments and safeguards. Thus 'mineral oil' (in certain forms) was added to the list of acknowledged substances with carcinogenic potential as long ago as 1914, and in Britain experimental skin cancer was produced in animals with shale oil in 1922. Later in that decade the carcinogenic action of unrefined mineral oil was demonstrated also in animal tests.

In a study of the cause of mule spinners' cancer in cotton mills investigations showed that solvent extracts and certain other fractions of mineral oils were highly carcinogenic to mouse skin. This led to the drawing up of a specification for highly refined white oils to be substituted.

In the UK investigational research on behalf of the petroleum industry has been supported by the Institute of Petroleum, and in 1967 a programme was set up to work in parallel with a Medical Research Council study which produced a report* drawing attention to the fact that the components in certain mineral oil fractions believed to be responsible for promoting skin cancer were polycyclic aromatics (PCA).

Polycyclic aromatic compounds consist of four to six fused aromatic rings, and it was shown that tumours could develop if PCA-containing materials were applied to animal skin at regular intervals for prolonged periods, with care taken to ensure that the oil is not removed from the skin between applications.

These findings led to the Institute recommendations in 'Mineral Oil and Skin Cancer' (1969) for the use of solvent-refined oils or oils which had received a similarly severe refining treatment to reduce the PCA content, and also the adoption of better hygiene and work practices. Since that time the principles underlying the safe use of mineral oils have been incorporated into various guidance notes and codes of practice of the Institute: for example, the IP Code of Practice for Metal Working Fluids, 1979.

Knowledge of, and identification of the potential health hazards of various materials is gained by a number of methods, which are complementary. These include direct clinical observation, animal testing, and more recently epidemiology, all of which have both their own aims and difficulties.

Much basic groundwork has resulted from clinical observation, in which links with occupational factors are identified, and once a causal relationship is known appropriate safeguards can be promulgated. If the cause and effect are only weakly linked this may present a difficulty, particularly where the substance is new or still undergoing development. Biological or animal testing, therefore, can play an important screening role by giving early warning of a potential hazard, since these tests enable exposures to be given under scientifically controlled conditions but, in order to accelerate and accentuate findings, at dosages which can be many times the actual exposure which occurs in the human field. It has been recognized, therefore, that such results, while being indicative, are not necessarily extrapolatable to man or to the conditions under which he works.

Epidemiology, which has been defined as the study of the determinants of the incidence and prevalence of disease in human populations, has therefore come to the fore as such a study technique. In this the disease incidence in a population group (e.g. employees in refineries, or in oil distribution occupations or whatever else the group of interest is) can be determined on a comparative basis with nationally compiled disease statistics for the population as a whole, such comparison being on an equivalent sex and age-adjusted basis. By tabulation of the observed disease incidence rate in the study group, compared with that statistically 'expected' from the age-comparable national

* The Carcinogenic Action of Mineral Oils; A Chemical and Biological Study: Medical Research Council Report SRS 306. HMSO. London, 1968.

population as a whole, a standardized mortality ratio (SMR) may be derived as explained later for each significant disease group or cause of death. This ability for direct comparison is of considerable value in determining whether there is a health problem in a particular group of individuals, or in a given industry or occupational category. It is therefore a very useful health research technique, further details of which will be given in the end section of this chapter. First, however, the basic methods of ensuring health safety in the handling and processing of petroleum materials in the industry will be outlined.

HEALTH AND HYGIENE IN THE PROCESSING OF PETROLEUM

The principal hazard in the refining, blending, and storage of petroleum is the flammability of crude oil and its products. (See Chapter 32.) The potential health and hygiene hazards that may be encountered present few problems, but these should be understood. A characteristic of refinery plant is its design essentially as a series of enclosed systems, so that exposure to its hydrocarbon or other process streams is normally minimal. Nevertheless, it is essential to ensure that all persons having to deal with these processes are aware of both the hazards and the precautions to be taken.

Some crude oils, and various process gas or liquid streams in refinery plant, may contain hydrogen sulphide (H_2S) at levels which will give rise to dangerous or lethal concentrations if there is a release or escape, and this is dealt with in the next section. Likewise chemicals, catalysts, and additives used in refineries may have their specific toxicity hazards, which require appropriate safe handling and protective working conditions in accordance with the safety guidance given by their suppliers.

Hydrocarbons in general have only low to moderate acute toxicities, though under prolonged and repeated exposure without adequate hygiene precautions, some—particularly of the higher boiling category—can give rise to chronic effects. Both acute and chronic aspects should be guarded against by following appropriate procedures. These are dealt with below.

Hydrogen Sulphide

Hydrogen sulphide exposure is considered to be one of the major industrial hazards to be guarded against in the petroleum industry. Because it may be encountered widely in a number of the upstream operations (including drilling, production, and refinery operations, though not in the refined products handled through an oil distribution terminal or depot), it will be dealt with first.

Sour crudes as handled in many producer operations and transported and received at a refinery can liberate appreciable amounts of hydrogen sulphide which, if inhaled, is highly toxic and lethal even in low concentrations. H_2S formation can also occur by breakdown during certain process operations of other sulphur compounds present even in 'sweet' crudes. Thus a number of both liquid and gas process streams in a refinery (e.g. crude still and catalytic cracker overhead and reflux streams, gas fractionator streams, hydrotreater recycle gas streams and off-gases) will have significant H_2S contents.

Hydrogen sulphide has a disagreeable odour characteristic of rotten eggs, but quickly deadens the sense of smell. This may lead to a false feeling of security, since disappearance of the smell, after it has been first noticed, may be due to an *increase* rather than a reduction in concentration.

The following guide to the effects on persons exposed to various atmospheric concentrations of H_2S gives some indications of the danger.

Measured in air by volume:

50–100 ppm	Eye and respiratory tract irritation after exposure of 1 hour.
200–300 ppm	Marked eye and respiratory tract irritation after exposure of 1 hour.
500–700 ppm	Dizziness, headache, nausea, etc. within 15 minutes; loss of consciousness and possible death after 30–60 minutes exposure.
700–900 ppm	Rapidly produces unconsciousness, and death occurs a few minutes later.
Over 1000 ppm	Apparent death (but see comment later) is instantaneous.

The concentration of H_2S in the air above, or in vapour coming from, an H_2S-bearing liquid can be very high. For example, the concentration of H_2S measured in vapours coming out of the ullage opening of a tank receiving crude oil of 70-ppm H_2S liquid content can be as high as 7000 ppm by volume. Heated bitumens in storage may also evolve hazardous concentrations of H_2S in the vapour space of a tank and in the vicinity of the gauging hatch, requiring precautions to be taken (See IP Bitumen Code).

Precautions Against H_2S

Breathing apparatus of the self-contained positive pressure type should be available for all persons who may be exposed to a dangerous concentration of H_2S. For plants whose streams contain high concentrations of H_2S, consideration should be given to the provision of escape-type respirators for use in emergency.

Hydrogen sulphide is heavier than air and may in calm conditions accumulate in dangerous concentrations in depressions, sumps, pits, or enclosed spaces. Wind direction should be taken into account by those approaching or working at a location where such gas may be expected. Tank gaugers, for example, should not stand downwind of hatches when sampling or dipping. Where the presence of H_2S is suspected, persons carrying out work should wear suitable breathing apparatus and, if appropriate, safety belts with lifelines, to permit easy rescue should the need arise. They should be attended by an additional person who should have immediately available suitable personal protective equipment. This person should stand by at a safe distance to render assistance or call for help in case of need. H_2S detectors and alarms should be considered in critical situations.

Persons overcome by H_2S should be removed at once to fresh air in a gas-free area (taking care that the rescuer protects his own safety by wearing appropriate breathing apparatus). If the victim is unconscious and not breathing, mouth to mouth artificial respiration should be applied immediately and

continued without interruption until normal breathing is restored. Apparent death from H_2S is not irreversible, since prompt and efficient artificial respiration may restore life.

Types of Exposure to Petroleum, its Intermediate Streams and Products

Exposure may be by inhalation, ingestion, aspiration, skin contact, or eye contact.

(*i*) *Inhalation*

Inhalation of a vapour, mist, or particulate material into the lungs may produce local irritation of the respiratory tract, or systemic effects from absorption into the blood-stream, which can include asphyxiation. Where a hazard could exist due to inhalation of a substance, guidance is given on the recommended exposure limits at work in the form of a Threshold Limit Value (TLV), usually given as the airborne concentration in parts of vapour or gas per million parts of air volume (ppm), but also as mg/m^3. (The definition of TLV has been given in Chapter 25.)

Where a TLV is applicable it should be observed, for example, by increased ventilation if necessary or dispersion to an appropriate level or, in circumstances where this may not always be practicable (e.g. in entry to a tank or vessel in the course of gas-freeing), by the use of appropriate protective breathing apparatus.

In the UK TLVs are listed by the Health and Safety Executive in a published annual Guide Note, EH 15.

The factors governing exposure to the vapour of petroleum materials are outlined below.

(*ii*) *Asphyxiation*

Asphyxiants interfere with the normal supply of oxygen to body tissues and with their essential functions.

Simple asphyxiants act by the dilution of atmospheric oxygen below the level required for regeneration of the blood-stream; examples are nitrogen, carbon dioxide, hydrogen, and very light gaseous hydrocarbons such as methane or ethane, so long as these are free from hydrogen sulphide.

Chemical asphyxiants damage the oxygen-carrying capacity of the blood, even though the oxygen supply itself may be normal. Examples are carbon monoxide, which combines more readily than oxygen with the haemoglobin in the blood and thus reduces the capacity of the haemoglobin to take up oxygen, and H_2S which exerts an asphyxiant action by causing respiratory paralysis.

(*iii*) *Effects of inhaling concentrations of petroleum vapours*

This section deals with petroleum vapours from materials which are H_2S-free.

Comparatively small quantities of petroleum vapour can, when inhaled, dull the sense of smell and cause symptoms of dizziness, similar to intoxication, with

headache and irritation of the eyes. These effects can occur at concentrations well below the lower flammable limit, but their absence should not be taken as an indication of the absence of a flammable mixture.

The vapour of petroleum in high concentrations can lead to narcosis and anaesthesia, and then suffocation if the concentration is high enough, or if the duration of exposure is sufficiently prolonged.

The effects of various concentrations of petroleum vapour in air are roughly as follows:

0.2% vol (2000 ppm)	Irritation of the eyes, nose, and throat; dizziness and unsteadiness within half an hour.
0.7% vol (7000 ppm)	Symptoms as of drunkenness within a quarter of an hour.
1.0% vol (10 000 ppm)	Rapid onset of drunkenness, symptoms which may lead to death.
2.0% vol (20 000 ppm)	Paralysis and death occur very rapidly.

Light materials such as gasolines have sufficiently high vapour pressures to allow a hazardous build-up of vapour in poorly ventilated or confined areas, particularly where there is spillage.

Kerosines and heavier products have sufficiently low vapour pressures to prevent a hazardous build-up of vapour at ordinary ambient temperature. Nevertheless, under conditions of poor ventilation and high temperature, a hazardous concentration of vapour can build up.

In all cases a safe working atmosphere should be provided by gas-freeing before entry into confined spaces, vessels and tankage without breathing apparatus. Safe levels for entry and working without breathing apparatus are tabulated in the IP Marketing and Refining Codes.

(*iv*) *Vapours from liquefied petroleum gases* (*LPG*)

These vapours also cause narcosis and in high concentrations produce anaesthesia, though this is less pronounced than with the vapours of higher boiling-point materials such as gasolines, naphthas, etc., as dealt with above.

(*v*) *Petroleum gases*

The lighter hydrocarbon gases (methane, ethane, ethylene) when H_2S-free have no appreciable physiological action, except when present in sufficient concentration as to lower the oxygen content of the air, in which case systemic effects arise simply from oxygen deprivation. (See under Oyxgen Deficiency.)

(*vi*) *Emergency action*

Asphyxiation cases should be moved to fresh air, kept warm and at rest, and if unconscious given oxygen. If breathing stops, artificial respiration should be given.

Ingestion of Petroleum Liquids

Ingestion (swallowing) is not usually serious, since taste and smell limit the amount swallowed, and in general petroleum materials have a very low order of toxicity when taken internally (i.e. orally).

The ingestion, however, of petroleum liquids may produce irritation of the mouth and the gastro-intestinal tract. These effects are more pronounced with the higher products such as gasoline and kerosine. The main hazard following accidental ingestion is aspiration of liquid into the lungs (see below). (Since children are more susceptible than adults, such a warning is particularly important to domestic users, to ensure that products are clearly labelled and kept out of reach.)

If petroleum products have been swallowed, the patient should be sent to hospital or medical attention should be sought immediately. Vomiting should *not* be induced.

Aspiration

Aspiration is the introduction of liquid into the lungs. The low viscosity of petroleum liquids such as gasoline and kerosine presents a serious aspiration hazard. Even small amounts of these materials can produce rapidly developing severe (even fatal) pneumonitis.

Aspiration can result after ingestion of a liquid if vomiting occurs, particularly if the person involved is unconscious or semi-conscious, and as stated above concurrent or subsequent aspiration is the more serious aspect of ingestion. Because of the aspiration danger, if a petroleum liquid is swallowed, no attempt should be made to induce vomiting, and medical aid should be obtained immediately.

Eye Contact

Eye protection should always be used where there is a possibility of spray, mist, or splashing reaching the eyes; however, accidental eye contact with unheated hydrocarbons is not generally a serious problem. Where there is eye contact with a petroleum substance, severe smarting of the eye may be caused, with irritation of the conjunctiva. The immediate treatment should be to wash the eyes with copious quantities of water for at least ten minutes. A few drops of sterile medicinal liquid paraffin may also be applied and may be repeated in a few hours. If irritation persists medical help should be sought.

Eye contact with chemicals and other substances used in a refinery should be treated in accordance with the suppliers' instructions.

(i) Skin Contact

Contact with the skin by petroleum and chemicals may result in both acute and chronic effects.

The systemic toxicity of petroleum hydrocarbons through skin contact is low, and absorption of these materials through the skin is not a rapid process. Hence normal good working practice to avoid prolonged and repeated skin

contact is sufficient to prevent acute toxicity being a problem. Chronic local skin affects can arise on contact with petroleum materials of varying types, but these can also be avoided by taking sound precautionary measures as described in the next section.

The effects of prolonged skin contamination with petroleum liquids, and the protective measures are as follows:

(ii) Skin Contamination with Petroleum Liquid

Petroleum liquids, especially the lighter fractions, are fat solvents, and contact with them tends to remove the natural protective properties of skin fats. Thus they tend to act as primary skin irritants that de-fat and dry the skin. Continued exposure to such liquids may induce dermatitis.

Prolonged contact with heavier fractions, either direct or through oily clothing, may lead to oil acne—the irritation of the hair follicles, evidenced by blackheads, pimples, and pustules. The heavier fractions from crude oil, and higher boiling-point oils derived from cracking-type processes, contain complex polycyclic aromatic hydrocarbon compounds as already described. Certain of these, on prolonged and repeated contact with the skin, are known to be carcinogenic. Such heavy oils may on long exposure cause warty growths which may be skin cancer or which may progress to skin cancer if not treated. Skin cancer is fortunately rare and is avoidable by observing the good personal hygiene measures (see below) that are necessary to avoid dermatitis and similar skin conditions.

The levels of PCA in various fractions and products are influenced by refining separation processes, such as extraction and fractionation, which reduce the PCA in some streams and concentrate them in others:

solvent extraction reduces to a low level the PCA content in refined lubricating oil products and concentrates it in the aromatic extract oils;

fractionation of cracking and pyrolysis streams concentrates the PCA in the heavy residues and tars. Examples of these are the cycle oils and residues from catalytic cracking, and the heavy residues from steam cracking.

(iii) Hygiene Precautions for the Safe Handling of Petroleum Liquids

Prolonged and repeated contact with the skin and the adverse effects described above may be avoided by keeping high standards of industrial and personal hygiene. The following precautions should be taken to avoid or minimize direct skin contact:

(1) Adequate protective clothing, which should include suitable gloves, should be worn. Clothing that has become soaked with oil should be removed, and parts of the body which have been in contact with oil should be thoroughly washed with soap and water. Overalls or other protective clothing should be changed as necessary, and should be dry-cleaned or laundered before re-use.

(2) Contaminated rags and tools should never be put into overall pockets.

(3) Good washing facilities should be provided with suitable proprietary hand cleansers and clean towels. Hands should be washed thoroughly before and after going to the lavatory and before eating or drinking.
(4) Degreasing fluids or products such as gasoline, kerosine, white spirits, etc. or chemical solvents should not be used for cleansing.
(5) Barrier creams may be used, but no assumption should be made that they protect the skin fully from direct exposure to oils or other fluids. Such creams, however, make eventual washing easier and more effective. 'Re-fatting' creams after washing may be of benefit in cases of dryness of the skin.
(6) Any scratch or cut should receive prompt first aid, since broken skin is more susceptible.
(7) Medical advice should be sought in the case of any abnormality such as discoloration, soreness, itching, swelling, or warty growths.

Aromatics Including Benzene

(i) Acute effects

Aromatic hydrocarbons can be absorbed readily into the body via inhalation and/or skin absorption.

In common with other volatile hydrocarbons, the lower boiling aromatic hydrocarbons (benzene, toluene, xylenes, ethyl benzene, etc.) exert an acute narcotic effect, and the inhalation of a sufficiently high concentration can result in acute intoxication, loss of consciousness, and eventual death.

The liquids cause local de-fatting and irritation of the skin and, if contact is repeated or prolonged, may lead to blistering and dermatitis. Aromatics are irritating to the eyes and to mucous membranes, and eye injury can result from accidental eye contact.

The normal precautions to avoid inhaling hydrocarbons and their contact with skin and eyes should be followed with hydrocarbon mixtures that contain aromatics.

(ii) Chronic (long-term) effects—benzene

Benzene has toxic properties which do not occur with other aromatics. Prolonged and repeated high exposures can cause: (1) bone marrow damage leading to blood disorders of varying severity, which are usually reversible after removal from further exposure, and (2) more rarely leukaemia. Such cases are associated with exposures of the order of 100 ppm or more, many times the occupational TLV.

Small amounts of liquid may be absorbed through the skin, but the chief route of entry to the body is by inhalation. All unnecessary exposure to benzene therefore is avoided, atmospheric concentrations are kept as low as possible, and individual exposures are controlled to below the TLV.

Benzene is present to a limited extent in gasolines, in concentrations not normally exceeding 5 per cent, and the appropriate precautions for handling gasoline should prevent any substantial exposure to benzene.

For further information, refer to the joint IP/CIA publication, *Health*

Precaution Guidelines for Benzene Exposure in the Petroleum Refining and Chemical Industries including Bulk Distribution. Also—*Toxicity Review of Benzene.* Fielder *et al.* UK Health and Safety Executive. HMSO, 1982.

Other Health Hazards

(*i*) *Oxygen deficiency*

The necessity to provide a safe working atmosphere before entry into any confined spaces, vessels, or tankage whether for inspection, cleaning, or repair has been stated in Chapter 32, and the 'work permit' system whereby this is ensured has been described.

In the case of hydrocarbon vapours this is achieved, after the vessel or tank is emptied and isolated by removing or blanking off all connections, by the process of 'gas-freeing'. Details of how this is carried out, and checked by gas detector equipment to safe limits are given in the IP Marketing and Refining Safety Codes.*

There is, however, another hazard to guard against, apart from hydrocarbon vapour concentrations before entry into a confined space, and this is due to a possible *oxygen deficiency*. Thus the normal air breathed contains 21 per cent of oxygen by volume. An oxygen deficiency (i.e. below 18–20 per cent) may result from, for example, steaming-out procedures, inert gas purging, welding and burning operations in confined poorly ventilated spaces, tanks, or other vessels. Suitable breathing apparatus should therefore be worn unless the space has been and remains adequately ventilated, and a responsible person has tested and certified it as safe for entry without breathing apparatus.

(*ii*) *Lead alkyl compounds*

Anti-knock compounds such as lead alkyls, e.g. tetramethyl lead (TML) and tetraethyl lead (TEL), used in the petroleum industry, are toxic and flammable. However, safe procedures and the appropriate protective clothing and breathing equipment have been developed for working with these compounds in their concentrated form. The rules and regulations laid down for their handling must be adhered to in their entirety.† Reference should be made to the appropriate publications issued by the manufacturers, from whom advice can also be obtained, and, in the UK, to the Control of Lead at Work Regulations, 1980.

In gasoline, lead alkyls are diluted about two thousand times, so that the opportunity for absorption of appreciable quantities through the human skin will not arise. Furthermore, the vaporization of tetra-alkyl leads from such low concentrations in gasoline is insignificant under the conditions required for the safe and normal handling of motor fuels.

* The 'gas-freeing' process, and the 'permit to work' system which it includes, will also ensure that the vessel does not contain a flammable atmosphere, so that work with tools which could provide a source of ignition (i.e. 'hot-work') can safely proceed; this is described in Chapter 32.

† A distinction may be made between the effects of exposure to the tetra-alkyl leads in concentrated form prior to blending and to those concentrations present after blending into motor fuels.

For these reasons the distribution and use of leaded gasolines as a motor fuel do not involve a significant exposure to lead, except during entry for cleaning and repair into tanks which have contained leaded products, in which case accumulated sludge and scale can contain dangerous amounts of lead. Again, for this purpose the full recommendations of the manufacturer of the lead alkyl should be followed in their entirety. These precautions include the removal from and subsequent disposal of the sludge and scale.

(*iii*) *Other additives, chemicals, etc.*

A wide variety of substances under this heading have been introduced over the years. It is necessary that their toxic and other properties are known and properly understood so that they can be handled safely.

(*iv*) *Catalysts used in refining*

The above remarks apply also to the use of catalysts. The hazard presented may be flammable (pyrophoric), toxic, corrosive, irritant, and in certain cases carcinogenic.

The use of the catalysts may concentrate trace elements and/or produce compounds which are themselves hazardous. Unnecessary exposure to catalysts, spent catalysts, and related substances therefore should be avoided. Manufacturers and licensers supply data on the properties of the catalysts and recommend the precautions to be taken.

(*v*) *Disposal of chemical and oily waste*

Disposal of chemical waste by dumping must not be carried out without full consultation with the appropriate public authorities. The waste must be classified as to type of hazard and should be properly labelled. All despatches should be accompanied by appropriate instructions.

Disposal calls for great care in the choice of site or the other means to be used. The following factors should be considered:

(1) Access and proximity of the public,
(2) Toxic properties,
(3) Contamination of underground water supplies,
(4) Effect on adjacent areas,
(5) The reactivity of different wastes and the products of these reactions, if at any stage they were to be brought together. An example would be the co-mingling of a spent sulphide solution with acidic material, with consequent liberation of H_2S.

Petroleum Product Safety for the Consumer or Industrial User

The basic health and hygiene precautions to be taken by employees working with petroleum materials in the petroleum industry itself have been described in the preceding section. Many, but not necessarily all, of these precautions are applicable to those who are handling or using these products in other

industries, or even domestically, although the degree and frequency of contact may be lower.

It is not necessary in a work of this nature to outline separately consumer guidances, but it should be noted that oil companies in marketing these products have drawn up and made available Guides to Health and Safety which describe the conditions necessary to ensure that such products will be safe and without risk to health *when properly used*. An important principle in this is that the products are used only for the purpose for which they are intended. An obvious dangerous mis-use would be the use of petrol for cleaning the hands, clothing or, for instance, vehicle parts, or for lighting fires. A sensible precaution in the home is always to keep and store petroleum products out of reach of children. Such products should be kept only in properly labelled containers, and never put into containers which have contained food or drink, which could be a danger to unsuspecting children or adults.

In addition to the individual company guidance literature, the Institute of Petroleum also puts out guidance notes on health hazards and precautions. Examples of these include 'Chapter 2 "Health Precautions" of the IP Bitumen Code (Part II), June 1979', and the 'IP Code of Practice for Metalworking Fluids, 1978'. The latter covers both mineral cutting oils and synthetic metal working fluids. An IP prepared 'Health Guide to Products' is being considered for possible publication.

Confirmation of Hygiene Precaution Measures and the Assessment of Occupational Health

In prescribing, as in the preceding sections, health and hygiene precautionary practices, it is of obvious interest to determine their adequacy. In this connection, the use of epidemiology has been described at the beginning of this chapter as being a valuable modern investigative procedure. The next section outlines the principles of epidemiology and briefly summarizes some of the results obtained in the petroleum industry.

EPIDEMIOLOGICAL STUDIES

The role of epidemiology in monitoring the health of defined population groups (in this instance, for example, those working with petroleum, or with its products) has already been mentioned. It is of particular value in helping to determine whether any occupational or environmental exposure or practice, or for that matter aspects of life-style such as smoking, diet, or drinking habits, etc., may give rise to ill health. Thus, by comparison with standardized population health data, which may be either in terms of 'morbidity' (the prevalence rate of various diseases and illnesses), or in terms of mortality data for the various classified disease groups, such studies enable a statistical assessment to be carried out to determine whether patterns of potential risk are detectable that could require further detailed investigation.

An advantage of the epidemiological approach is that whereas clinical studies are carried out on cases of disease that have occurred, from which it may not be always clear or easy to assess whether these are indicative of an

excess or problem area, epidemiology which studies disease statistically takes as its starting base a total study population that is well defined (e.g. all those working in a refinery between set dates), technically referred to for such a purpose as 'the population at risk'. It then follows up the status of all in that study group to establish a *rate of incidence* for each disease or disease grouping that can then be compared with equivalent standardized population data to arrive at a 'standardized mortality ratio' as explained below. Such comparison would be meaningless if age differences and distribution are not taken into account, and it is therefore carried out on an an age-specific, i.e. adjusted age equivalent basis. The standardized population data used will be its all-male subdivision if the study is to be on males. An example of epidemiology has been its bringing out of the link between smoking and lung cancer.

Mortality surveys lend themselves particularly to carrying out such studies on a 'retrospective' basis, since by the systematic collation and tracing both of living status and of death certification data for those who are deceased, it is possible to build up from records an assessment covering many past years; this is of advantage in enabling data to be obtained on groups of persons who have already had long years of service in a particular job category or industry, including those who have retired, and also on groups who have varying periods of such service (1-5 years, 6–10, 11–15, 16–20, 20 plus years, etc.). Records of illness are rarely available in such fullness to enable 'morbidity' studies to be carried out on such a retrospective, or historic basis. It is therefore usually necessarily the case that morbidity studies have to be carried out on a 'prospective' or forward basis. Such a study in which illness is recorded as it occurs may therefore not yield results until a very considerable period will have elapsed.

Both types of study have their value, but, as in the review of health factors there is an obvious benefit for early information to become available, there has been a general move amongst epidemiologists to studies of the patterns of mortality of those working in or who have worked in various industries, which are then compared with those not so occupationally engaged. Support for such a move has come about both nationally (e.g. in the UK the Health and Safety at Work Act 1974 has placed the onus on an employer to identify whether his workers are exposed to risk), and by international organizations such as the World Health Organization.

The petroleum industry has been in the forefront of this epidemiological development, both in North America (under the auspices, among others, of the American Petroleum Institute) and in the UK, where three studies sponsored by the Institute of Petroleum and carried out by the Institute of Cancer Research have recently been published (1980–1982). An overview by Doll of these studies has been published in the *Proceedings of the Institute of Petroleum 1982 Annual Conference*, 'Health and Hazards in a Changing Oil Scene' (Wiley). Other countries, and doubtless other industries, will follow this example of an epidemiological approach.

The three IP sponsored studies, available in full at the Institute, are the following:

(1) An Epidemiological Survey of Eight Oil Refineries in the UK (Rushton and Alderson). 23rd March 1980.

(2) An Epidemiological Survey of Oil Distribution Centres in Great Britain (Rushton and Alderson)—Final Report 1982.
(3) An Epidemiological Survey of Maintenance Workers in London Transport Executive bus garages and Chiswick Works.—Final Report (Rushton and Alderson). 22nd March 1982.

Methodology

The outline scope of these studies, two of which covered the two main sectors of the UK petroleum industry, namely refineries and bulk oil distribution installations, while the third (the study of diesel bus maintenance personnel in London Transport workshops) was selected to cover an important user group occupationally working with diesel fuels, mineral cutting oils and lubricants, is given in Table I.

For each of the defined study populations the status as living or deceased at the study cut-off date of 31 December 1975 was traced, and all causes of death broken down according to some 180 standard categories as listed in the WHO International Classification of Disease groups to obtain the figure of the observed deaths 'O', for each disease grouping. These were then tabulated and compared with the calculated age equivalent expected deaths 'E' derived from the statistics of the UK National (or where appropriate, regional) 'all male' register.

The ratio of these two numbers, O/E, is the 'Standardized Mortality Ratio' (a ratio above 1.0 being an excess while below 1.0 it is a deficit), and a further step is then carried out mathematically to determine whether, for the respective numbers entailed, any deviation between O and E, and therefore the O/E ratio itself, is statistically significant, or falls into the statistically non-significant category. This form of analysis, including further breakdown into sub-groups, including job type, age, length of service, date of joining, etc., is of great value in identifying whether there are areas of potential concern in respect of any health factor, which would require follow-up, e.g. by further clinical review, etc. of all the circumstances.

The latter is of importance, since practitioners of epidemiological procedures stress that the calculation of a 'statistically significant excess' in the mathematical sense as above does not necessarily indicate significance in the clinical sense, i.e. such a finding may be just a chance association rather than a 'causal' relationship, or be a result of life-style rather than an occupational factor.

Results

The tabulation given (Table I) cannot encompass the full breakdown into causes of death of the original studies, but information has been chosen to give a broad picture suitable for illustrating a number of the main features. For such a purpose, the table focuses on the following categories: (1) all causes of death; (2) the main causes of death in all three studies; (3) deaths from cancer, in view of the prevalence of the belief among the general public that industrial and environmental factors are contributory; (4) for comparison two accidental death categories.

The high trace rate achieved is first to be noted as a requisite achievement

(99.8 per cent in the first two studies). In respect of (1) 'all causes of death' it will be seen that the number of observed deaths in all three study populations is well below the expected, with SMR ratios of 0.84 0.85 as compared to the general population. This is often referred to as the healthy worker effect, and is to be seen in category (2), 'main causes of death' (the figure of 0.99 for ischaemic heart disease in the second study was close to that of the general population and was overviewed by Doll, who considered that it reflected some aspect of life-style, rather than occupation). Doll quotes other experts, e.g. Fox, as suggesting that the 'healthy worker effect' will work off in the course of time, and figures for this have been suggested that are of the order of five to up to 10 to 15 years, with some never completely disappearing; this is a reason why for sound evaluation a *total* study population should be defined, and then all in it, including early leavers and those who retired, should be followed up.

In 3(a) the finding in all three study populations of a marked deficit in the number of 'deaths from all neoplasms' is of particular interest, in view of the mentioned growth of focus on cancer in all its aspects and recognizable concern whether there are occupational contributory associations.

Because lung cancer is the most prevalent of the various cancer forms in modern society and had been previously postulated as a hazard in the industry, the very significant deficits shown in 3(b) (SMR ratios of 0.78 and 0.80) in the two petroleum industry studies are also of note. Though it has been questioned whether restrictions in smoking during work at petroleum premises may provide some explanation, there is no firm evidence that overall smoking in the course of the day is substantially different from that in any other population sector.

The healthy worker effect has been mentioned above in relation to general disease, and taking out lung cancer from the 'deaths from all neoplasms' in 3(a) gives SMRs for the aggregated other cancer forms much closer to the norm level of the general population (99 per cent and 95 per cent in the first two studies; 87 per cent in the diesel maintenance study). Doll expresses the view that this is to be expected, since the healthy worker effect that can occur with other diseases cannot be expected in the case of malignant disease, for which an SMR of around unity could be regarded as normal. The remaining examples in 3(b) are illustrative of the whole. The findings for cancer of the stomach and intestines showed a slight excess overall in the refining study, though the numbers are reported as well below the level having statistical significance. The figures for brain cancer showed no excess as had been reported in one (US) study, and those for leukaemia did not show an excess, though exposure to high benzene concentrations has been shown to cause an excess of certain leukaemia types (see the earlier section on chronic benzene effects). In his overview Doll notes that the studies do not appear to point to any hazard, or give support for there being any excess mortality from gastro-intestinal cancer, or that exposure to petroleum produces cancer of the brain, lymphoma (not dealt with in this abridged digest), or leukaemia.

The figures in all three studies for cancer of the skin showing a very significant deficit (with no deaths from scrotal cancer), are of particular relevance, in view of the historical linkage between skin cancer (epitheliomas) and contact with certain, particularly unrefined, heavy mineral oils, and the replication of this effect in animal skin painting tests discussed previously. The

TABLE I

UK Oil Related Epidemiological Studies (Ruston and Alderson, 1980, 1982)

Scope of the studies	Study of eight UK refineries (1980)			Study of oil distribution centres (1982)			Study of London Transport maintenance workers (1982)		
Number of employees in study, past and present including leavers and retired	34 781			23 358			8684		
Locations covered	Eight UK refineries in England, Wales, and Scotland			Over 700 distribution centres throughout the UK			The main London Transport diesel bus maintenance centres		
Period covered	25 year period (1.1.1950 to 31.12.1975)			25 year period (1.1.1950 to 31.12.1975)			(1.1.1967 to 31.12.1975)*		
Number (percentage) untraced	73 (0.2%)			52 (0.2%)			194 (2%)		
Mortality by categories	Observed (O)	Expected (E)	SMR (O/E)	Observed (O)	Expected (E)	SMR (O/E)	Observed (O)	Expected (E)	SMR (O/E)
1. All causes of death	4406	5296	0.84	3926	4632	0,85	705	836	0.84
2. Listed main death causes									
Cerebro-vascular disease (strokes)	408	452	0.90	374	431	0.87	58	74.4	0.78
Ischaemic heart disease (heart attack)	1428	1590	0.90	1377	1384	0.99	244	277	0.88
Bronchitis	253	393	0.64	240	359	0.67	50	64.7	0.77

3. (a) Deaths from all neoplasms (cancers)	1147	1286	0.89	1002	1157	0.87	216	226.8	0.95
3. (b) Some illustrative breakdown within 3(a) above									
Lung cancer	416	633	0.78	384	483	0.80	102	101	1.01
Cancer of the stomach	167	161	1.04 NS	123	144.5	0.85	26	25.5	1.02 NS
Cancer of the intestines	84	79	1.07 NS	57	72	0.79	10	13	0.76
Brain and other CNS	36	45	0.80	39	37	1.07 NS	7	6	1.2 NS
Cancer of the nasal cavities and sinus	7	3	2.24	None	—	—	Below reporting level		
Cancer of the skin	None			5†	8.5†	0.59	1— Below the expected		
Melanoma	14	7	2	3	5	0.6	Below reporting level		
Leukaemia	30	32	0.94	28	27	1.04 NS	7	5	1.5 NS
4. Miscellaneous accidental deaths									
Accidental deaths from fire and explosion	12‡	6	2	7§	4.2		Below reporting level		
Accidental road deaths	110	102	1.08	75	70	1.07	8	10	0.8

NS = non-significant.
* Earlier records not available.
† In this study includes the melanoma figures below.
‡ Including one outside of work.
§ Including two outside of work.

studies' findings are therefore an important reassurance as to modern refining treatment and the effectiveness of the health and hygiene precautions that have been cited. The excess of melanoma reported in the refining study (14 observed versus 7 expected out of 34 708 employed) was statistically significant despite the very small numbers. It is of interest that melanoma is one of those few cancers that are becoming more common in the world (Doll), and in all white-skinned but not other populations; thus it has been attributed to the exposure of the skin to the ultra-violet light of the sun. A further check made by the researchers at the two centres where the excess mainly occurred showed no common factor in the persons concerned.

The two sets of figures in (4) of accidental deaths are given to serve as a contrast, and have been referred to in other chapters of this book. It should be noted that in the studies described, *all* deaths occurring are included in the comparisons, whether likely to be associated with work or outside of it, since this is the only method by which a standardized mortality ratio can be reached. It will be seen even from the briefness of this discussion how epidemiological work can provide a valuable perspective in the study of health and assessments of risk that is attainable by no other investigative technique.

This can be heightened by the contrast of similar studies of a comparable nature one with another (e.g. as between the UK and US), since if an excess of one disease form or another is found in one study, but is found not to be present in other studies of an equivalent scope and methodology, this is further evidence of the unlikelihood of there being a causal link.

Weaver, in such a comparison in the *Proceedings of the Institute of Petroleum 1982 Annual Conference* has further highlighted this, in a review of epidemiological studies of refineries in the US with that in the UK. In none of the six was there the finding of a consistent significant excess of mortality from a specific form of cancer, arguing strongly against the presence of an occupational problem for this disease in the industry.

Weaver's paper has commented that certain studies in the US have been reported on the basis of proportionate mortality ratio (PMR). This differs from the standardized mortality approach, in that a PMR study is carried out on collected records of deaths only, requiring no data other than the age, sex, and cause of death of known dead. As there are no data relating these back to any defined total study population, i.e. the total population at risk, which they should be related to, there is also a danger that such a list will be incomplete, e.g. if taken only from active union membership lists, in which case there might be practically no deaths identifiable from the various common heart, respiratory, or circulatory, etc. diseases. In such a circumstance, since the listing as used will be taken as the 100 per cent starting point in calculating PMRs, if one or more of such causes of death are low because of incompleteness, other causes, e.g. cancers, can be overweighted and appear to give a high PMR, even though there need be no true excess. Doll has commented on this in his overview.

Proportionate mortality studies which can accentuate excesses/deficits, therefore do not give information as to whether overall or cause-specific mortality rates are high or low, unlike the SMR approach which deals with actual rates, a point not always understood, e.g. in reporting by the media.

However, PMR studies are quick and easy to perform, since no systematic

external tracing is involved as in an SMR study, and in the sense that their results may suggest a need for further study, they have been classed as 'Hypothesis-Generating', as compared to the more definitive 'Hypothesis-Testing Studies', using standardized mortality ratio and a carefully established study population, that have been described in this chapter.

For fuller reading on this subject as a whole, the 11th World Petroleum Congress 1983 Round Table Discussion 7, Paper 4, 'Epidemiological Surveys in the Oil Industry', Leese, W. L. B. and Jones, P. (John Wiley & Sons Ltd.) should be consulted.

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